NITROGEN TRANSFORMATIONS AND GASEOUS LOSSES FOLLOWING FERTILIZATION OF A SLASH PINE PLANTATION

By

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To Helen

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Nitrogen transformations, movement of elements, and gaseous N losses were monitored during 128 days following the application of two N fertilizers to a 23-year-old slash pine (Pinus elliottii Engelm) plantation. Treatments consisting of urea and ammonium sulfate at 0, 100, 200, 300, and 400 kg $N.ha^{-1}$, were applied directly to the forest floor in plots, arranged in a randomized block design. Gaseous NH_3 volatilization was measured for two methods of application, i.e., spraying of solutions and spreading of solid or prilled fertilizer. In addition, cations, C, P as well as N species were analyzed from soil samples taken 2, 4, 8, 12, 16, 21, 32, 64, and 128 days after treatment application.

Denitrification was assessed by measuring the evolution of N_2O from two subsequent field installations utilizing ammonium nitrate in addition to urea and ammonium sulfate N sources.

Precipitation throughfall was recorded on the experimental site during the whole experimental period.

Urea fertilizer was hydrolyzed in the forest floor within 21 days of application and the major part of the urea was undetectable 4 days after fertilization.

Soil acidity was reduced two pH units by application of urea at the highest level, and acidity was increased about one unit by the application of ammonium sulfate at the same level.

Water extracts of samples from urea treated plots had very low concentrations of cations including NH_4^+ compared with extracts from ammonium sulfate treated areas. The differences in extractability of cations following fertilization were thought to reflect the increase in soil cation exchange capacity resulting from urea fertilization, and the decrease in cation exchange capacity following application of ammonium sulfate. Water-soluble C in soil samples was much greater following urea fertilization than that extracted from the soil following ammonium sulfate applications. Although abundant NH_4^+ was detected following applications of both urea and ammonium sulfate, little or no NO_3^- was detected in extracts, during 128 days following fertilization. This indicated that even though conditions for nitrification were improved, especially by urea fertilization, little or no NO_3^- was detected in the soil.

Ammonia volatilization was about 3% of applied N. The greatest flux of N_2O from ammonium nitrate applied at 200 kg $N.ha^{-1}$ was 11 g $N_2O\text{-}N.ha^{-1}.day^{-1}$ and the flux from urea applied at 400 kg $N.ha^{-1}$ was 53 g $N_2O\text{-}N.ha^{-1}.day^{-1}$ for a brief period following heavy rainfall 54 days after fertilization.

Cumulative throughfall for 50 days was 500 mm and the linear accumulation of rain following fertilization explained a significant

part of the variation in the exponential decrease in NH_3 volatilization.

The rapid decline in the concentration of N, C, cations, and P in the soil, following fertilization, was explained by regressions incorporating treatment and time since fertilization parameters.

Using a N_2:N_2O ratio of 10:1, denitrification losses would represent approximately 1% of the applied N. Combined losses from NH_3 volatilization and denitrification were still small, amounting to < 5% of applied N. When a not unrealistic ratio of 100:1 was used, losses from ammonium nitrate during 100 days following fertilization would represent 29% of the applied fertilizer.

Because losses from denitrification of urea or ammonium sulfate were found to be very small in this study, low recovery of N from ammoniacal sources found in similar studies on deep sandy soils in similar climates is therefore likely to be explained by leaching.

INTRODUCTION

Nitrogen (N) deficiency is probably the most widespread nutrient deficiency in forest ecosystems (Bengston, 1973; Rennie, 1979; Pritchett, 1979), and responses to the addition of N fertilizers have been observed in many coniferous ecosystems. Use of N fertilizers is increasing worldwide and will probably continue to do so for the remainder of the decade, particularly in North America (Bengston, 1979).

In the southern U.S., the flatwoods ecosystem incorporating large areas of native and plantation slash pine stands represents a significant forest resource. In addition to the Spodosols, other flatwoods soils likely to show improved tree growth following N fertilization have been identified (Pritchett and Smith, 1974; Fisher and Garbett, in review).

A recent study (Mead, 1971) has indicated that only about 50% of fertilizer N applied to a slash pine plantation is recovered. Sarigumba (1974) demonstrated greater leaching of NH_4^+ and other cations following fertilization with ammonium sulfate than using urea fertilizer.

With an increasing demand for a diminishing fossil feedstock for manufacture of N fertilizers it is imperative that the most efficient use be made of N fertilizer applied to forest stands. A fuller understanding of the soil reactions and N transformations which result from the use of different sources of fertilizer N will allow tree crop managers to become more effective N users.

The consequences of the use of current N sources, methods, and rates of fertilizer applications can be better understood by studying the movement of N fertilizers in the field, where many otherwise difficult to control environmental parameters are integrated. Field losses including those from denitrification of N can also be assessed from a well replicated installation, incorporating N fertilizer treatments of greatest interest. Measurement of potential losses from denitrification need to be assessed in order to compare losses from this transformation with those from leaching. In addition, the need to ascertain denitrification rates from soils in general has been highlighted by Wollum and Davey (1975). The effects of rainfall frequency and intensity on subsequent leaching losses and anaerobic conditions produced as a result of soil saturation need to be considered in the proposed field studies. This study was undertaken to examine from field installations within the slash pine ecosystem the consequences of different N fertilizer applications, and specifically the objectives were

(1) To monitor initial reactions and the subsequent sequence of N transformations following fertilization.

(2) To determine the extent of hydrolysis, ammonification, nitrification, and denitrification in an acidic sandy Spodosol.

(3) To compare N transformations resulting from the use of two commercial N fertilizers; ammonium sulfate and urea.

(4) To correlate N, carbon (C), and mineral cation movements following fertilization.

(5) To assess the relative roles of leaching and denitrification as sinks for applied N fertilizers.

LITERATURE REVIEW

Nitrogen Fertilization of Forests

Many forest ecosystems are located on what might be regarded as poor agricultural land and their productivity is less than optimum. Furthermore, in a time when the land base is diminishing and demands for forest resources and products are growing, ways of increasing wood production need to be rigorously studied (FAO-IUFRO, 1973). Recognition of naturally occurring growth limitations and their corrections, along with the successful introduction of rapid growing and efficient tree species on a world-wide basis, would increase forest productivity of many areas.

Conifers in native and exotic stands have shown marked response to fertilization in many parts of the world, particularly to additions of phosphorus (P) and N (Pritchett, 1969). Pritchett and Smith (1974) reported significant growth responses of slash pine to additions of N and P in southeastern U.S. coastal plain. Heilman and Gessel (1963) demonstrated the responsiveness of Douglas-fir (*Pseudotsuga menziesii* (Mirb.) Franco) to urea fertilization. They found a response lasting 2-10 years after fertilization of N-deficient Douglas-fir stands, and a long-term improvement in N nutrition due to enrichment of the N cycle. Rennie (1979) suggested that N deficiency was still the most widespread nutritional problem in forests, and in Canada interest and efforts were being increased in N fertilization. Swan (1974) summarized reports on a number of Canadian forest species which showed responses to N fertilization. He reported white pine (Pinus strobus L.) plantations in Quebec province established on old farmland which have shown responses to additions of potassium (K) and N. Other species in eastern Canada that have responded to fertilization include red spruce (Picea rubens Sarg.), balsam fir (Abies balsamea (L.) Mill.), jack pine (Pinus banksiana Lamb.), and red pine (Pinus resinosa Ait.). Fertilization in western Canada concentrated on Douglas-fir where expectations for response are similar to those described by Heilman and Gessel (1963) for the adjacent North American stands.

The importance of N, P, and other elements to exotic plantations of radiata pine (Pinus radiata D. Don.) in Australia was reported by Raupach (1967) and Woods (1976) and for maritime pine (Pinus pinaster Ait.) by Boardman (1974). Radiata pine responded to additions of P in superphosphate, and responses were greatest on deeply podzolized sands when competition for moisture by other vegetation was not severe. In addition, an impermeable subsurface horizon within 90-150 cm of the soil surface endowed a site with a mid-range productivity potential. Similar conditions were required for the response of maritime pine to phosphatic fertilizers; in addition this species was more tolerant than radiata pine of a low soil P status. Radiata pine showed dramatic responses to small incremental applications of N in South Australia (Woods, 1976).

Responses by radiata pine in New Zealand to applications of superphosphate (Conway, 1962) and to N (Ballard, 1977) have been substantial. Radiata pine, amongst many other exotic conifers grown in South Africa, has shown similar responsiveness to both N and P additions (Schutz, 1975). In the colder climates of Europe and Scandinavia, considerable tree growth response to urea and ammonium nitrate forms of N have been reported (Baule and Fricker, 1970; Holmen et al., 1976).

Nitrogen fertilization of forests has increased substantially in recent years, especially where a favorable cost-benefit ratio exists for the operation (Bengston, 1979). Rates of fertilizer N applied ranged from between 200 to 400 kg N.ha^{-1} for Douglas-fir (Gessel, 1968) in the Pacific Northwest to between 60 to 120 kg N.ha^{-1} for slash pine plantations in the southeastern U.S. (Pritchett and Gooding, 1975).

In boreal forests, a sustained response for longer than 10 years to 488 kg urea-N.ha^{-1} was achieved, but a more temporary 2-year response resulted from 112 kg N.ha^{-1} applied to black spruce (Picea mariana (Mill.) BSP.) in early Canadian trials (Armson et al., 1975). In the Scandinavian region response to N fertilization depends on the tree species and the type of forest floor generated under the stand. Tamm (1969) indicated that 5-year growth response increased with N dosages up to 400 kg N.ha^{-1}. On sites with thin humus layers, ammonium nitrate has been an N source superior to urea (Tamm, 1968). Woollons and Will (1975) suggested that sustained growth response could be achieved by two successive annual applications of 112 kg urea-N.ha^{-1} to radiata pine in New Zealand. Slash pine responded to combined applications of N and P or to P alone on very poorly drained or imperfectly drained sites in Florida (Pritchett, 1979).

Sources of fertilizer N used vary from region to region, depending on forest type, local availability of fertilizer materials, and costs associated with application to the forest. In Sweden, ammonium nitrate increased growth of Scots pine (Pinus sylvestris L.) up to 50% more than that obtained from an equivalent amount of urea-N (Möller, 1973). The most commonly used fertilizer in Canada was urea (Swan, 1974)--yet some forests in eastern Canada showed a greater response to ammonium nitrate and calcium nitrate than to urea (Weetman and Algar, 1974). The lower reported response to urea-N was most likely due to the higher degree of biotic immobilization compared with ammonium sulfate, calcium nitrate, or calcium cyanamid (Wollum and Davey, 1975).

Although urea appears to be the most widely accepted N source for forest fertilization, significant quantities of ammonium sulfate and ammonium nitrate are used, especially when their cost per unit of N is favorable compared with urea.

The Nitrogen Cycle

The forms (or species) of N in the biosphere are interconnected by a series of reactions which together comprise the N-cycle. Photochemical reactions for the most part make up the atmospheric section, whilst biologically mediated chemical reactions complete the aquatic and terrestrial parts of the N-cycle.

The many transformations of N species are represented in a simple fashion in Figure 1 (National Research Council, p. 23, 1978).

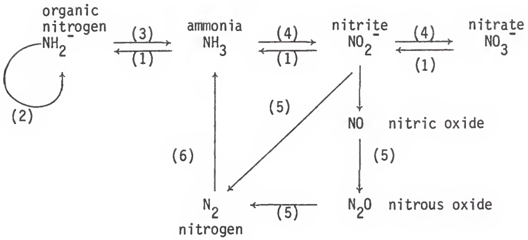

Figure 1. Nitrogen cycle and major transformations (National Research Council).

The six major processes or transformations illustrated in Figure 1 are as follows:

(1) assimilation of inorganic forms--principally ammonia and nitrate--by organisms to form organic N;

(2) heterotrophic conversion of organic N by microorganisms;

(3) ammonification, the decomposition of organic N to ammonia (mineralization);

(4) nitrification, the oxidation of ammonia to nitrate and nitrite;

(5) denitrification, biological and chemical reduction of nitrate to nitrous oxide (N_2O) and nitrogen (N_2) under anoxic conditions; and

(6) N fixation, the reduction of N_2 to ammonia and organic forms of nitrogen by microbes.

Although other reactions contribute to the N cycle those above constitute the major transformations.

Nitrogen in Forest Soils

The total amount of N in a soil depends largely on the type of soil and environmental conditions. Some peaty soils have greater than 2.5% N while the total N in mineral subsoils will be a fraction of that amount.

Average N concentration for surface mineral soils range from 0.03-0.4% (Bremner, 1967) and decrease with depth. Ninety to ninety-eight percent of N in surface soils is organically combined (Bremner, 1965a) with the balance existing as ammonium (NH_4^+), nitrite (NO_2^-), or nitrate (NO_3^-) N. In forest soils with a strongly developed forest floor, organic N can comprise more than 98% of the total in the surface horizons. Some estimates of the N content of the forest floor (Table 1) demonstrate how this element accumulates and is stored in this component of the forest stand. Nitrogen in other soil horizons might exceed the total accumulated in the forest floor, but the N nutrition of the forest is likely to be determined by the ease or rate at which litter and other soil organic N are decomposed. Florence and Lamb (1974) suggested that productivity of radiata pine was inversely related to litter accumulation within plantations on sandy soils. The rate of litter accumulation is a function of soil and parent materials, for ponderosa pine (Pinus ponderosa Laws.) (Welch

Table 1. Range of N content of forest floors of several coniferous ecosystems.

Forest type and species	N in the forest floor, kg·ha^{-1}	Reference
Boreal		
Black spruce	890-1210	Roberge et al., 1970 Weetman and Webber, 1972
Red spruce-fir	1460	Weetman and Webber, 1972
White fir	880	Wollum, 1973
Temperate		
Birch-spruce	3190	McFee and Stone, 1965
Old growth mixed conifers	1390-2050	Gessel and Balci, 1965
Immature Douglas-fir	190-220	Gessel and Balci, 1965
Lodgepole pine	330	Moir and Grier, 1969
Ponderosa pine	340-600	Welch and Klemmedson, 1973
Virginia pine	240	Metz et al., 1970
Temperate-Sub-tropical		
Loblolly pine	350	Wells, 1971
	260	Metz et al., 1970
Slash pine	280	Huang, 1978
	360	*Kushla, 1978

*Note: Data from an independent study on my experimental area.

and Klemmedson, 1973). For most forest ecosystems it is also influenced by associated vegetation, available soil moisture, and rate of decomposition.

Climatic conditions determined by geographic latitude determine the rate of litter accumulation. Bray and Gorham (1964) demonstrated that up to 12 $t.ha^{-1}.yr^{-1}$ fell in tropical rainforests and this amount declined linearly with increasing latitude to 2-6 $t.ha^{-1}.yr^{-1}$ for cool temperate regions. Frequency of forest fires will influence the amount of N stored in forest litter. Yet Wells (1971) reported no long-term N losses in soil organic matter associated with periodic and annual prescribed fires in a loblolly pine forest. Accumulation of litter can be rapid for the first 10 years after fire, but for some forest types accretion in the forest floor continues for centuries (McFee and Stone, 1965). The colder climates of the boreal forests in Canada and Scandinavia result in large accumulations of N in the forest floor, and an associated slow litter decomposition has been held responsible for general deficiencies in available N in these forests (Weetman and Webber, 1972). Burning of the boreal forest, although resulting in an instantaneous loss of N, actually causes an increase in soil N mineralization due to amelioration of the acidic conditions which inhibit litter decomposition and other microbial activity (Viro, 1974). Moist tropical rainforests often have a greater annual litter fall than the boreal forests but litter accumulation is offset by high rates of decomposition and mineralization of C and N resulting in a redistribution of these elements into the surface mineral horizons (Olson, 1963).

Forests growing on sandy soils which contain few weatherable minerals and little or no clay capable of fixing NH_4^+ will have a significant portion of the ecosystem N contained in the forest floor. Stimulation of litter decomposition by the many agencies reviewed, and by human and animal disturbances, can result in increased mineralization of N and greater uptake of this element by all components of the ecosystem. There may be a loss to the ecosystem if the disturbances are sufficiently gross to result in surface run-off, deep leaching, and/or the evolution of N gases.

Biological Assimilation and Plant Uptake

It is generally accepted that nitrification is of minor importance in natural forest ecosystems (Richards, 1974; Attiwill, 1979). Consequently NO_3^- is detected at very low levels in many forested ecosystems, especially coniferous ecosystems. This could mean in addition to low nitrification rates, that NO_3^- is being rapidly assimilated by microflora and fauna, is being taken up by vegetation, or lost by leaching and denitrification. Plant roots may absorb NH_4^+, NO_3^-, urea, or even simple amino acids (Viets, 1965). Youngberg (1978) has shown that between 0.3-9.9% of N mobilized from a number of forest floor types was organic in nature, perhaps indicating that a small part of N supply to forest trees was organic.

In agricultural soils when urea or liquid ammonia is applied, the rise in pH following ammonium carbonate formation enhances microbial transformations, including nitrification, resulting in NO_3^- rich soils. Pritchett et al. (1959) found that freshly cultivated acidic soils had higher nitrifying capacity than if the soil had been undisturbed. They related increased NO_3^- production to soil organic matter, soil texture, and cultural practice. The finer textured soils, and those with greatest organic matter, in addition to cultural inputs, had highest NO_3^- production. In a lysimeter study, addition of 500 kg urea-N.ha^{-1} to a forest soil did not result in large increases in nitrification (*Tamm, 1979), indicating that some forest soils are well buffered against chemical disturbances, and have developed a very dominant ammonifying microbial population.

Ingestad (1970) reported that special attention must be paid to the ratio of NH_4^+ and NO_3^--N in culture solutions, for birch seedlings. This researcher maintained optimum nutrient levels by adjusting conductivity and solution pH with NH_4^+ and NO_3^- additions. He found each ion to be important for the growth of birch seedlings. White spruce (Picea glauca (Moench) Voss) and radiata pine exhibited greater growth and N uptake when treated with NH_4^+ than with NO_3^-, whether they were grown in solution culture or soil (McFee and Stone, 1968).

The net uptake of applied N fertilizers by forest species will depend on the source of fertilizer and the forest ecosystem involved. Overrein (1969b) found that 16% of a 100 ppm urea-N addition to Norway spruce (Picea abies (L.) Karst.) and Scots pine (Pinus sylvestris L.) was taken up by these trees. Mead (1971) using ^{15}N-labelled ammonium sulfate found that only 10% of the applied ^{15}N was detected in roots and above-ground parts of slash pine 19 months later.

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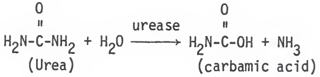
*Note: Personal communication.

Nitrogen Transformations

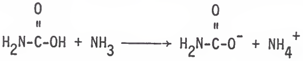
Ureolysis

The many transformations of N compounds are represented diagrammatically in Figure 1. In addition, the ammonification or hydrolysis of urea is referred to as ureolysis. This reaction is mediated by the specific enzyme urease found in natural soil systems primarily in association with organic matter and clay (Burns et al., 1972a,b). The first step in ureolysis is the formation of carbamic acid and is depicted in equation [1].



$$\underset{\text{(Urea)}}{H_2N\text{-}\overset{\overset{O}{\|}}{C}\text{-}NH_2} + H_2O \xrightarrow{\text{urease}} \underset{\text{(carbamic acid)}}{H_2N\text{-}\overset{\overset{O}{\|}}{C}\text{-}OH} + NH_3 \qquad [1]$$

The NH_3 formed in equation [1] reacts with carbamic acid removing a proton to form NH_4^+ and carbamate; this is depicted in equation [2].



$$H_2N\text{-}\overset{\overset{O}{\|}}{C}\text{-}OH + NH_3 \longrightarrow H_2N\text{-}\overset{\overset{O}{\|}}{C}\text{-}O^- + NH_4^+ \qquad [2]$$

The products of this reaction form ammonium carbamate by ionic bonding, as in equation [3].

$$NH_4^+ + H_2N\text{-}COO^- \longrightarrow \underset{\text{(ammonium carbamate)}}{H_2COONH_4} \qquad [3]$$

The remaining $-NH_2$ can follow the same sequence of reactions with water to result in ammonium carbonate, depicted in equation [4].

$$H_2N\text{-}COONH_4 + H_2O \longrightarrow 2NH_4^+ + CO_3^= \longrightarrow \underset{\text{(ammonium carbonate)}}{(NH_4)_2CO_3} \qquad [4]$$

Equation [1] indicates that water is necessary, but is considered non-limiting in most soil systems.

Pseudo-first order reaction kinetics have been demonstrated for the hydrolysis reaction by Simpson and Melsted (1963), who found no effect of level of applied urea on rate of hydrolysis. Crane (1972) found that rate of reaction was linearly related to urease concentration but curvilinearly related to urea concentration. This finding was supported by early work of Laidler and Hoare (1949) who recorded linear increases in ureolysis in response to additions of urea and then a subsequent decline at higher concentrations. Rates of ureolysis (Crane, 1972) were measured at between 1440-2560 ppm $N.g^{-1}$ $soil.day^{-1}$, and compared favorably with rates reported by Roberge and Knowles (1966). Soil buffered the reaction at a lower rate than that found in aqueous systems and temperature increases resulted in earlier completion of the reaction: 6 days at 25°C versus 25 days at 2°C (Crane, 1972). Under conditions of heavy rainfall and with highly permeable sands, some penetration of unhydrolyzed urea might be expected; this was reported by Sarigumba (1974) and Soubies, as cited in review by Kiss et al. (1975). Sarigumba and Fiskell (1975) reported complexing of urea and soil organic matter before ureolysis was completed and a subsequent slower rate of hydrolysis, which helps to explain pseudo-first order kinetics reported earlier (Simpson and Melsted, 1963). These workers (Sarigumba and Fiskell, 1975) also demonstrated inhibition of ureolysis in two soils by the use of phenylmercuric acetate, an inhibitor reported by Douglas and Bremner (1970). The use of toluene or γ-irradiation as an enzymatic inhibitor has highlighted the fact that urease exists (or pre-exists) in the soil, since toluene treated soils effectively hydrolyze urea additions utilizing accumulated urease (Conrad, 1940; Roberge, 1968). Lloyd and Sheaffe (1973) claimed that soils limiting in carbon for microbial proliferation hydrolyze urea at a steady rate. With no increase in microbial population urease activity was still detected and they concluded that urea additions were hydrolyzed by accumulated urease.

Ammonia Volatilization

The primary consequence of ureolysis is the step-wise formation of ammonium carbonate (see equation [4]) which subsequently gives rise to increases in soil pH.

Ammonium carbonate is unstable in soil and is likely to undergo dissociation as shown in equation [5],

$$(NH_4)_2CO_3 \rightleftharpoons 2NH_4^+ + CO_3^= \qquad [5]$$

and gaseous ammonia (NH_3) volatilization will result under certain conditions. Ammonium and NH_3 exist in equilibrium with aqueous ammonia (NH_{3aq}) in equation [6].

$$\underset{\text{ammonium}}{NH_4^+} \rightleftharpoons H^+ + \underset{\substack{\text{aqueous}\\\text{ammonia}}}{NH_{3aq}} \rightleftharpoons \underset{\substack{\text{gaseous}\\\text{ammonia}}}{NH_3} \qquad [6]$$

The distribution of NH_4^+/NH_3 will be primarily a function of pH. In acid forest soils there is generally no shortage of protons (H^+) to drive the reaction to NH_4^+. The ratio of $NH_4^+:NH_3$ in aqueous solution is shown in Figure 2 (Crane, 1972).

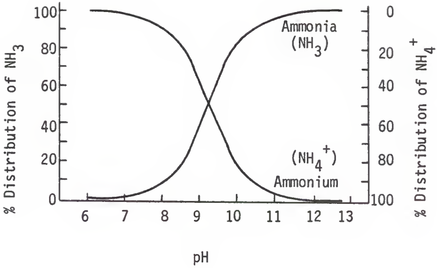


Figure 2. Relative distribution of ammonia and ammonium at 25°C (Crane, 1972).

From Figure 2 it is clear that with increasing pH, the likelihood of volatile loss of NH_3 increases.

Following urea fertilization, ammonium carbonate is formed and is basic in nature resulting in a rise in pH and the chance of subsequent NH_3 volatilization.

Sources of protons (H^+) will drive the reaction (equation [6]) to the left and reduce NH_3 losses. Interactions of water, clay, organic matter, and hydroxyl groups (OH^-) with NH_3 also can result in reduced volatilization (Mortland, 1958).

Two contrasting effects on volatilization are reported following burning of the forest: Volk (1970) reported half as much volatilization on the burnt area which he attributed to reduced ureolysis. Raison and McGarity (1978), studying the influence of plant ash on transformation of N fertilizers, found that in moist ash alone urea and potassium nitrate were unaffected, but 63 and 70% of N applied as ammonium sulfate was volatilized from autoclaved and non-autoclaved ashes, respectively, over a 4 day period. Applications of ash to soil resulted in increased volatilization which they attributed to pH increases, saturation of exchange sites with basic cations, and stimulation of urease activity.

Watkins et al. (1972) found that application of urea resulted in a rise of 2 units in soil pH, and applications of urea to the forest floor doubled NH_3 losses when compared with applications to mineral soil. This would suggest that the site of maximum ureolysis is intimately associated with the forest floor--a concept which was supported by Derome (1975), who found peak urease activity in a zone above the litter-mineral soil interface. In addition he found a strong positive curvilinear relation between medium pH and urease activity, minimal activity at pH less than 4.5 and strongly increasing activity at a pH greater than 5.5.

Many workers have investigated and compared effects of urea preparations and mixtures, including prill size and coatings and methods and rates of applications, with inorganic N sources upon NH_3 losses from the soil. Nommik (1973) compared large (2060 mg) pellets with standard (2-4 mg) prills and found no long-term effect of prill size on NH_3 losses after 28 days. The losses were 20 and 22% for the large and small pellets, respectively. He also found losses were cut by 50% by additions of ortho-phosphoric acid solution or fine-crystalline ortho-boric acid to the large pellets.

Application of a concentrated ammonium sulfate solution with 8% water to a calcareous soil (pH 7.6) resulted in maximum NH_3 losses of near 50% of applied N (Fenn and Escarzaga, 1976), which supported earlier work of Gasser (1964) who found elevated losses when ammonium sulfate was applied to calcareous soils.

Fenn and Escarzaga (1976) found maximum losses at all temperatures and N application rates when soils contained 13-30% water. Matocha (1976) found 18% NH_3 losses from urea applied to a soil (pH 6.0) at 600 kg $N.ha^{-1}$ compared with less than 1% for ammonium sulfate, ammonium nitrate, or sulfur-coated urea.

In detailed lysimetric studies using ^{15}N-urea, Overrein (1968, 1969a) investigated leaching and gaseous losses from soil columns cut from the forest. He agreed with Crane (1972) that there were increased NH_3 losses with higher levels of applied urea-^{15}N. Total NH_3 losses amounted to 3.5% of applied N, with a marked drop in losses after the 6th day from the highest urea applications (500 and 1000 kg urea-$N.ha^{-1}$). Overrein (1967) suggested that adsorption of NH_4^+ by the raw humus resulting from ureolysis prevented excessive losses of NH_3 from application rates up to 250 kg $N.ha^{-1}$, and that the adsorption capacity of the forest floor was saturated beyond this level of fertilization. Approximately a quarter of the NH_3 lost was released from the forest floor organic materials.

Gasser (1964) studied NH_3 losses from different soils as affected by N source, soil type, and method of N application and temperature. High soil temperature (25°C) resulted in early losses of NH_3 compared with cold temperature (5°C). Sandy loam soils lost 14-22% of applied N as NH_3 compared with 2-4% for clay soils.

There was little difference in NH_3 lost when urea was applied in prilled or crystalline form or in solution on all soils.

Mineralization-Immobilization

The mineralization of urea, or ureolysis, was discussed in the previous section. Other organic forms of N in the soil undergo decomposition and oxidation, resulting in inorganic molecules. The first step in this process--conversion to NH_4^+--should be referred to as mineralization, with subsequent inorganic transformations being specifically named. Many texts include all the subsequent oxidative transformations in the term mineralization. Another approach is simply to call the first step in the mineralization process ammonification.

Assimilation of inorganic N molecules into biological tissues is called immobilization, and this process occurs simultaneously with mineralization. Richards (1974) reported that the mineralization-immobilization cycle in the soil is dependent on energy in the form of readily decomposible organic materials. If the supply of organic matter is rich in N, decomposition will result in the accumulation of inorganic N or net mineralization, and plants which require the inorganic N species can take up or assimilate this surplus. When raw plant or organic materials are supplied to the soil system the microbial populations expand to colonize the new energy source and utilize the surplus inorganic N ions, resulting in net immobilization of N.

It is assumed that within the mineralization-immobilization cycle higher plants cannot successfully compete with microorganisms for the inorganic N (Richards, 1974).

In forest ecosystems with highly acidic soils fungi are prominent chemoheterotrophes, with the phycomycetes considered the most important, although most groups are represented in isolation studies (Richards, 1974).

From the preceding comments it can be seen that the ratio between energy supply (carbon) and N within any soil amendments will determine the subsequent net mineralization or net immobilization process. A comprehensive review of factors affecting mineralization transformations was made by Harmsen and van Schreven (1955). Verstraeten, Vlassak, and co-workers, in a series of studies (1969, 1970a, 1970b, 1972) using incubation techniques, found that agronomic soils should be handled separately from forest soils for regression analysis between water-soluble carbon and mineralized N. They also found that sandy soils did not behave in the same way as loamy or clayey soils with respect to mineralization of nitrogen. Separation of analyses by vegetation type and soil texture class allowed application of chemical test data to determine an index of nitrogen availability.

Windsor (1958) reviewed a number of studies which investigated the percentage of N in organic materials commonly applied as soil amendments. He found that when the level of N in the material to be applied to the soil was greater or equal to 2% then this material was effective in supplying N to the soil.

The same effect is expressed by the carbon:nitrogen (C:N) ratio of the soil amendments. Windsor (1958) suggested that soils with a resultant high C:N ratio contain organic matter that has not been decomposed to the extent found in old cultivated soils. Hu et al. (1972) supported this finding; they studied several different litter materials and found readily oxidizable (soluble) carbon at greater levels in the least decomposed layers of the forest floor.

When N fertilizer materials are added to the soil a major "disturbance" to the existing C:N ratio takes place, giving rise to physical, chemical, and biological changes. It would be anticipated that a forest with a thick litter accumulation and a low N concentration would immobilize a large portion of the added fertilizer. Roberge and Knowles (1966) found little net immobilization in spite of a high C:N ratio in spruce humus materials. In a later study (Roberge, 1972), it was found that the more decomposed humus, with a narrower C:N ratio, held considerably more exchangeable NH_4^+.

In studying mechanisms of immobilization of urea N fertilizers, Roberge (1976) found that urea applied at 280 kg $N.ha^{-1}$ stimulated respiration of litter microbes, whereas ammonium nitrate or ammonium sulfate depressed respiration. Urea-N immobilized in this way may become available subsequent to the death and decomposition of microbial cells; some, however, may be complexed and held unavailable to plants for a sustained period, or be incorporated in the non-extractable part of soil N (Overrein, 1970). Mitsui (1967) claimed that the main mechanism of urea immobilization was associated with its ability to self-polymerize or combine with the decomposition products of organic matter. Urea may also be immobilized in the short term by clay adsorption mechanisms following salt formation (Broadbent and Lewis, 1964). Adsorption is unlikely to be important in the surface horizons of sand podzolic soils with less than 5% clay, where the exchange capacity is dominated by constant potential surfaces (Keng and Uehara, 1974). Rather, the rise in pH accompanying ureolysis will increase the pH-dependent cation exchange capacity and result in larger amounts of NH_4^+ on the exchange complex.

Stanford and co-workers (1955, 1972, 1973a) developed an incubation technique for assessing and indexing soils according to their ability to mineralize N and make it available for plant growth. These methods have been used to assess the impact of organic amendments to soils (Epstein et al., 1978) and to correlate indices generated in this fashion with plant uptake (Stanford and Legg, 1968; Stanford et al., 1973b).

The mineralization process may be directly enhanced by chemical amendments; Williams (1972) reported increased mineralization of acid humus following liming. Broadbent (1965) showed that N fertilization increased mineralization.

Knowles (1975, p. 53) summarized recent research utilizing fertilizer ^{15}N on the immobilization-mineralization process.

(1) At low pH with additions of NH_4^+-^{15}N to sterilized acid humus, transfer of ^{15}N to the organic fraction did not occur, but did occur at higher pH--demonstrating the pH dependent nature of the exchange complex.

(2) Additions of NH_4-^{15}N to non-sterile humus resulted in rapid transfer of ^{15}N, being more rapid in mull than moder or mor litter classes. Subsequent release of humus N as extractable NH_4^+ indicated that the "priming effect" had not taken place. But in a separate study:

(3) Immobilization of NH_4^+-^{15}N took place in the presence of added calcium carbonate and was in contrast to the "priming effect" observed following the addition of NH_4^+-^{15}N and NO_3^--^{15}N without liming.

(4) Priming of organic N was markedly greater than immobilization of NH_4^+-^{15}N for additions of NH_4^+ and NO_3^--^{15}N, but less for additions of urea-^{15}N.

(5) In general, the extent of immobilization of ^{15}N appeared to be urea > NH_4Cl > KNO_3, but applications of 50-400 ppm of NH_4^+-^{15}N resulted in the release of up to 1500 ppm KCl-extractable organic-N. Ogner (1972) reported mobilization of organic matter following urea fertilization to forest humus.

Nitrification

Nitrification is a term which collectively refers to the oxidation of NH_4^+ species to nitrite (NO_2^-) and/or nitrate (NO_3^-). Nitrification processes in soils have been reviewed extensively by Alexander (1965, 1977). Nitrification is a two step process and both steps are microbiologically mediated by obligate aerobic bacteria. Nitrosomonas is typical of the autotrophic organisms capable of oxidizing the reduced forms of N. Other bacteria, including some heterotrophes, are considered to be equally, if not more important, in this conversion. Focht and Verstraete (1977) listed a number of autotrophic and heterotrophic organisms capable of the process, which is represented below by equations [7] and [8].

$$NH_4^+ + 3/2\ O_2 \longrightarrow NO_2^- + H_2O + 2H^+ \qquad \Delta G° = -65\ kcal.mol^{-1} \qquad [7]$$

Oxidation of NO_2^- to NO_3^- is the second step in nitrification:

$$NO_2^- + 1/2\ O_2 \longrightarrow NO_3^- \qquad \Delta G° = -20\ kcal.mol^{-1} \qquad [8]$$

The second step is mediated by a group of organisms typified by Nitrobacter species.

A number of inorganic and organic compounds have been suggested as possible intermediates in nitrification (Table 2; Alexander, 1965). It has been demonstrated that many of these organic intermediates can be substrates for an oxidation pathway leading to NO_2^- formation in culture.

Table 2. Intermediates in nitrification (Alexander, 1965).

Inorganic	Organic
Ammonia (NH_3)	Amine (RCH_2NH_2)
Hydroxylamine (NH_2OH)	Amide ($RCONH_2$)
Hyponitrous acid ($H_2N_2O_2$)	N-Alkyl hydroxylamine (RCH_2NHOH)
Nitrous acid (HNO_2)	Oxime ($RCHNOH$)
Nitric acid (HNO_3)	Hydroxamic acid ($RCONHOH$)
	Nitroalkane (RCH_2NO_2)

The free energies for equations [7] and [8] would indicate that the oxidation of NO_2^- is favored over the oxidation of NH_4^+. Ammonification is considered the slowest step in the overall process from organic-N to NO_3^-. Since autotrophes are considered the major mediators in the process, the rate of supply of each N substrate in turn limits the overall process. Many environmental variables affect the process, but soil acidity probably has the most pronounced effect. In acidic soils, the activity of autotrophes is markedly reduced, even in the presence of adequate substrate. In pure culture, optimum pH is between 7.5 and 8.0. In soils, nitrification falls off rapidly below pH 6.0 and is negligible below 5.0 (Alexander, 1977). Nitrification can occur at a soil pH of 4.5 (Burger, 1979), and even at pH 4.0 (Richards, 1974), and this is important when considering the acidic nature of soils of pine ecosystems. Nitrification is generally much more prominent in soils covered with a mull forest floor compared with soils with a mor litter layer. The forest vegetation and associated litter, soil texture, and pH interact with climatic conditions to control the extent of nitrification in soils. The fact that NO_3^- is often only detected at very low levels in forest soils can be explained a number of ways.

(1) Nitrification is, in fact, occurring, but at a very low level.

(2) Nitrification is occurring but utilization of nitrate is so rapid by higher plants and microorganisms that it is chemically undetectable (no net NO_3^-).

(3) Nitrification is occurring but is lost by denitrification and leaching processes.

Another view held by Rice and Pancholy (1972) was that climax vegetation types inhibit the nitrification process. This view was supported by the fact that a forest soil when disturbed, limed, or cultivated, resulted in greater NO_3^- accumulation (Vitousek et al., 1979; Pritchett et al., 1959).

Soil moisture is critical for the process; either too little or excessive moisture results in no nitrification or a reduction of NO_3^- accumulation. Alternate wet and dry weather, typified by tropical summers, can result in highly fluctuating NO_3^- levels and low NH_4^+ (Greenland, 1958). Organic N is apparently readily ammonified in hot moist conditions and NO_3^- is periodically (almost daily) leached from the surface soil.

The optimum depth within a soil for nitrification to take place is likely to be governed by the combination of soil pH, aeration, availability of substrate and moisture, rather than depth per se.

The impact of fertilizer on immobilization-mineralization reactions carries over to the nitrification process. Changes brought about by fertilizer additions to soil pH will markedly affect subsequent nitrification. Additions of ammonium sulfate to acid soils is unlikely to result in increased nitrification, but the addition of urea with subsequent localized pH elevation, and solubilization of C, improves soil conditions and substrate supply for both autotrophic and heterotrophic nitrification. Roberge and Knowles (1966) reported such an effect 28 days following urea or ammonium carbonate fertilization.

It has been suggested only recently (Bremner and Blackmer, 1979) that nitrous oxide (N_2O) was generated during nitrification in moist soils. Nitrous oxide is generally considered to be an intermediate product in denitrification, so the conclusion by Bremner and Blackmer (1979) might be interpreted as simultaneous nitrification and denitrification in physically separate micro-environments within the soil.

Biological Denitrification

Denitrification within the scheme shown previously (Figure 1) consists of two processes, chemo-denitrification and microbially mediated denitrification. From the preceding discussion it can be seen that following nitrification, NO_3^- can be used either assimilatively, as a source of N for growth, or dissimilatively, as a terminal electron acceptor by combinations of fungi and bacteria when conditions of oxygen depletion occur. Nitrite is the main chemical species resulting from this process, and it in turn is substrate for further biological or chemical reduction. Cooper and Smith (1963) outlined what is generally accepted as the sequence of intermediates in biological denitrification, from their studies on a number of western U.S. soils. The sequence of products that they found is represented by equation [9].

$$\underset{\text{nitrate}}{NO_3^-} \longrightarrow \underset{\text{nitrite}}{NO_2^-} \longrightarrow \underset{\substack{\text{nitric}\\\text{oxide}}}{NO} \longrightarrow \underset{\substack{\text{nitrous}\\\text{oxide}}}{N_2O} \longrightarrow \underset{\text{nitrogen}}{N_2} \qquad [9]$$

Nitric oxide (NO) is not considered to be an important or stable intermediate; however, N_2O has been more precisely and accurately measured in recent years than other intermediates, and has been estimated to constitute 6% of the total denitrification products in agricultural soils (CAST, 1976). The ratio between N_2O and N_2 resulting from biological denitrification is discussed later in this section.

Brezonik (1977) reported a list of denitrifying micro-organisms, present in both soil and aquatic systems. Most denitrifyers are facultative aerobes, and survive in partially aerobic conditions, so denitrification in conditions of fluctuating oxygen levels in soils with anoxic microsites is microbially feasible. Other requirements for the denitrification process include neutral soil pH, a ready availability of carbonaceous substrates, and a suitable temperature regime. Alternate wetting and drying has been found to enhance decomposition of organic matter (Richards, 1974) which results in pulses of decomposition products moving through the soil in the wet phase of such a cycle. This relationship is of particular importance in tropical and subtropical climates with periodic intense rainstorms during hot summer months. Patrick and Wyatt (1964) found that alternate wetting and drying of the soil resulted in increased denitrification. Denitrification will occur in the temperature range of 5°C to 60°C. The optimum temperature has been reported to be near 35°C (Stanford et al., 1975; Focht and Chang, 1975) with a Q_{10} of about 2 between 15°C and 35°C. The optimum pH has been reported to be between 7 and 8 (Nommik, 1956) and denitrification was shown to decline rapidly under acidic conditions (Bremner and Shaw, 1958; Broadbent and Clarke, 1965).

The C:N ratio was discussed in connection with mineralization and immobilization of N in soils and litter. The optimum C:N ratio for the denitrification process, as suggested by de Haan and Zwerman (1976), can be derived from the stoichiometry in equation [10] shown below.

$$C_6H_{12}O_6 + 4NO_3^- \longrightarrow 6H_2O + 6CO_2 + 2N_2 \qquad [10]$$

From this equation the optimum ratio would be 1.3 mg of C for each mg of NO_3^- reduced to N_2. This is a very narrow C:N ratio of 1.3:1, but such a ratio was reported for agricultural waste-water by St. Amant and McCarty (in review, de Haan and Zwerman, 1976). This indicates that, although heterotrophic mineralization and autotrophic plus heterotrophic oxidation may occur with substrate C:N ratios from 10-30, denitrification would require a narrower ratio. Burford and Bremner (1975) investigated denitrification in relation to total organic C, mineralizable C, and water-soluble organic C. They found strong correlations between denitrification and all three measures of carbon, for a diverse collection of soils.

Nitrogen fertilization of agricultural lands combined with management practices which deplete soil C may result in additional deep leaching of NO_3^-, enrichment of groundwater, and pollution of adjacent streams. Vitousek et al. (1979) systematically examined the practices which could result in increased nitrification, NO_3^- accumulation within, and NO_3^- losses from forest ecosystems. They identified a total of eight processes which included N immobilization, delays in nitrification, lack of water for transport and plant uptake which act to reduce NO_3^- losses from forest sites. They concluded, however, that these processes were insufficient, except for plant uptake, to prevent losses from fertile forest sites, and hence such sites following forestry operational disturbances have the potential for high nitrate losses. The sites chosen for this study (Vitousek et al., 1979) did not include a representative site from the deep, acidic, sandy Spodosols upon which so much flatwoods coniferous forest occurs in the southeastern U.S. Increases in soil solution NO_3^- levels have been reported for a sandy flatwoods soil (CRIFF, 1977) following site preparation. Greater increases were reported in the same study from soil solutions sampled below an established slash pine plantation and adjacent prepared sites following urea fertilization. The extent of potential biological denitrification will depend upon the levels of NO_3^- and rate of nitrification occurring in the soil system. Therefore, this process will only occur following fertilization of the forest if NO_3^- is produced as a result of the operation. Simultaneous displacement of C with NO_3^- could lower the risks of pollution because denitrification could reduce the NO_3^- levels. This is more likely to occur following applications of urea than with ammonium sulfate fertilization for reasons previously reviewed.

Net denitrification losses can be measured by quantifying N_2O and N_2 gaseous losses from the soil. If the reaction in equation [9] does not go past the reduction of NO to N_2O, the measurement of N_2O will quantify the process. The acetylene blockage method has been used to show inhibition of the further reduction of N_2O, in culture studies (Yoshinari and Knowles, 1976), in soil slurries amended with ^{13}N (Smith et al., 1978), and in field studies (Ryden et al., 1979). Bremner and Blackmer (1979) reported the inhibitory effect of NO_3^- on the reduction of N_2O to N_2. However, it is neither desirable nor practical to use the acetylene blockage method in systems which generate the NO_3^- for denitrification. Walter et al. (1979) demonstrated that, in addition to N_2O reducation, acetylene also inhibited nitrification, thus diminishing the rate of supply of NO_3^- for subsequent denitrification. Therefore, to estimate total denitrification following additions of urea, or as a result of cultural treatment, some estimate of the ratio between N_2:N_2O evolved is needed, or a direct measurement of both N_2 and N_2O is required. Rolston and Broadbent (1977) measured both N_2O and N_2 in a Californian agricultural soil, irrigated and amended with straw and $^{15}NO_3^-$, and were thus able to determine the N_2:N_2O ratio. They found that the ratio was initially quite variable ranging from 1:1 to 40:1, but was generally close to 10:1 for significant periods of their experiments.

Ryden et al. (1979), in separate experiments, found essentially the same results as Rolston and Broadbent (1977). *Krottje (1979) has estimated the ratios for a number of south Florida soils and has found them to be between 10:1 and 100:1, depending on the soil.

Environmental and soil conditions which affect the N_2:N_2O ratio have been summarized by Focht (1974). They included soil pH, aeration, organic matter content, and temperature. Soil temperature and pH were found to have little effect on the ratio, but both had a profound effect upon the absolute rate of denitrification, as was reported earlier in this review. Soil aeration, however, as it was influenced by soil moisture, affected the ratio. Low concentrations of N_2O in soil had a dual meaning: (1) with unsaturated conditions it represents the major part of the gases arising from denitrification, but (2) in saturated soil it may be a minor component.

The total N loss via biological denitrification has not been reported for many forest soils. Overrein (1969b) was not able to detect denitrification in a boreal forest soil. Nommik (1956) measured potential losses of up to 50% of applied N in incubation studies using

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*Note: Krottje, P., personal communication.

forest soil materials. More often N balance studies result in the unexplained N losses allocated to denitrification. Many such studies in agricultural systems have reported denitrification losses between 10-20% of the added fertilizer (Broadbent and Clark, 1965). Direct measurements using sealed gas chambers resulted in losses between 20-70% of $^{15}NO_3^-$ applied to an agricultural soil and subjected to different irrigation schemes (Rolston et al., 1976).

Average total losses from agricultural soils have been estimated at 19 kg $N \cdot ha^{-1} \cdot yr^{-1}$ (Hauck, 1971).

In a recent model of a hardwood forest ecosystem (Swank, 1979) estimated denitrification losses were similar to those proposed by Hauck (1971) for agricultural soils.

To reduce losses of NO_3^- from fertilized crops it has been suggested by Goring (1962) to reduce or eliminate the NO_3^--N formation process of nitrification by the use of inhibitors, and considerable research has been conducted along these lines for agronomic crops. Another approach is to coat or mix fertilizer sources to reduce the rate of ureolysis, as in the case of sulfur-coated ureas. Such a coating reduces losses due to NH_3 volatilization, as well as serving as a controlled release of inorganic-N to the target crop. Broadbent and Clark (1965) claimed it was not economically feasible to use specially formulated fertilizers to reduce fertilizer losses due to denitrification even if losses to this transformation were 10-30% of applied N; however, these economics may be changed in an era of expensive feedstock for nitrogen fertilizer manufacture.

Chemo-Denitrification

In addition to biologically mediated denitrification of NO_3^-, several reactions have been proposed to account for non-biological losses of NO_3^--N. Chao and Kroontje (1966) reported that two of the intermediates in the nitrification pathway proposed by Alexander (1965)--hydroxylamine (NH_2OH) and hyponitrite ($H_2N_2O_2$)--were unstable in the presence of reduced iron (Fe^{++}). The stepwise reduction of these intermediates is represented by equations [11] and [12].

$$\left.\begin{array}{l} H_2N_2O_2 \\ NH_2OH \end{array}\right) + H^+ + Fe^{++} —— N_2H_5^+ + H_2O + Fe^{+++} \qquad [11]$$

$$N_2H_5^+ + H^+ + Fe^{++} —— NH_4^+ + Fe^{+++} \qquad [12]$$

Broadbent and Clark (1965) suggested that in acidic soil conditions nitrite was reduced to nitric oxide in a series of reactions summarized by equation [13].

$$2NO_2^- —— NO + NO_3^- \qquad [13]$$

Also working in acidic conditions Allison (1963) has suggested that modified forms of the Van Slyke reaction with ammonia or amino acids in nitrous acid would result in evolution of N_2, represented by equations [14] and [15].

$$NH_3 + HNO_2 \longrightarrow NH_4NO_2 + 2H_2O + N_2\uparrow \qquad [14]$$

$$R\text{-}NH_2 + HNO_2 \longrightarrow ROH + H_2O + N_2\uparrow \qquad [15]$$

Significant losses from chemo-denitrification have been reported by Gerretson and de Hoop (1957) for ammonium sulfate applied to acid sandy soil. Losses were about 30% of the applied N.

Under intensely anaerobic (reduced) conditions, NO_3^- can be reduced by a non-assimilatory pathway to NH_4^+-N (Buresh and Patrick, 1978). The conditions for chemo-denitrification--reduced soil conditions and an acidic medium--are often met in the flatwoods forest ecosystem. This would lead us not to discount the process of chemo-denitrification when assessing pathways of denitrification losses.

Leaching and Ion Exchange

Many highly productive ecosystems, the Pacific Northwest and the southeastern regions of the U.S. as examples, are subjected to intensive and prolonged periods of rain. The effect of rainfall following fertilization of such forest ecosystems can be measured by the rate of loss of nutrients from the forested ecosystem by leaching. Cole and Gessel (1965) measured a loss of 85% of the total N applied as urea to a coniferous forest floor in thirty days following fertilization. Little movement was detected after six months, and was similar to the untreated control. A fall application of 448 kg $N \cdot ha^{-1}$ as urea to a young second growth Douglas-fir plantation, without a well-developed forest floor resulted in elevated pH in the surface, increased nitrification after 3 months, and increased concentrations of basic cations in leachates (Otchere-Boateng and Ballard, 1978).

Urea applications, either as split doses or as a single application, to a silty Mollisol resulted in excessive NO_3^- leaching following heavy irrigation (Bauder and Schneider, 1979).

Cole and Gessel (1965) found greater leaching of N following ammonium sulfate fertilization than that measured following urea applications. Sarigumba (1974) also found more cations in leachates from a lysimeter experiment when ammonium sulfate was used as the N fertilizer, as compared with urea.

McColl and Cole (1968) proposed an overall mechanism of cation transport based on anion movement. Following urea fertilization the most prominent anion will be bicarbonate (HCO_3^-); in addition, negatively charged organic colloids will be increased and contribute towards cation transport. This latter mode of cation transport has been called ligand transport (Hingston et al., 1967).

Crane (1972) reviewed the cation exchange processes which resulted from applications of nitrogenous fertilizers. Additions of NH_4^+-N to the forest soil surface can result in an exchange depicted in equation [16].

$$\left|\begin{matrix} \mathrm{K}^+ \\ \\ \mathrm{Ca}^{++} \end{matrix}\right. + 3\mathrm{NH}_4^+ \longrightarrow \left|\begin{matrix} \mathrm{NH}_4^+ \\ \mathrm{NH}_4^+ \\ \mathrm{NH}_4^+ \end{matrix}\right. + \mathrm{K}^+ + \mathrm{Ca}^{++} \qquad [16]$$

This is an ionic exchange reaction but Hingston et al. (1967) suggested that both ionic and ligand exchange reactions were involved, and this contention was supported by Ogner (1972) who found increased organic matter mobilization following urea fertilization. Broadbent and Lewis (1964) and Ogner (1972) further suggested that NH_4^+ generated as a function of ureolysis following urea fertilization would be transported as the salts of the acidic groups of humic components, represented in equation [17].

$$\begin{array}{l} \text{R-COOH} \\ \text{R'-OH} \end{array} + 2\text{NH}_4^+ \longrightarrow \begin{array}{l} \text{RCOONH}_4^+ \\ \text{RONH}_4 \end{array} + 2\text{H}^+ \qquad [17]$$

Ammonium sulfate used as an N source provides an additional dimension to ionic exchange. Bolt (1976) suggested that anion exchange was limited to 1-5% of the cation exchange and that selectivity for sites with respect to different anions was much larger due to a lower degree of hydration compared to cations. When the sulfate ion ($SO_4^=$) was added it could be expected to be preferentially adsorbed compared with NO_3^- or chloride (Cl^-) ions. In this fashion, any small amount of NO_3^- loosely held on organic exchange sites would be displaced.

MATERIALS AND METHODS

Introduction

Field experiments were installed in a 23-year-old slash pine plantation, growing on an Ultic Haplaquod, in order to monitor movement of N in the soil profile and transformations of N fertilizers. Because it was not feasible to meet all the specific objectives in one installation, three field experiments were conducted on the one site.

Field experiment #1 was designed to examine the effects of N fertilization with urea and ammonium sulfate upon subsequent N losses via ammonia volatilization. In addition, movement of N in the soil profile was monitored by periodic soil sampling and these data were related to rainfall recorded on the site.

Field experiment #2 was installed one year after experiment #1 on a smaller area within experiment #1 boundaries and was designed to monitor nitrous oxide losses from the soil due to denitrification, following fertilization with urea and ammonium sulfate.

Field experiment #3 consisted of a small installation located adjacent to field experiment #2. The purpose of this installation was to expand the range of N fertilizer sources to include ammonium nitrate. It was installed 23 days after the installation of field experiment #2.

Experimental Location

In selecting an experimental site care was taken to identify an area which supported a well developed slash pine plantation. The site was also initially checked for gross variation in profile characteristics in order to identify a single pedon for the fertilizer treatments.

The site chosen for the field installations was located on private forest land approximately 8 kilometers north of the University of Florida campus, one and one-half kilometers north of U.S. highway 441, and bounded on the east by Florida road 121. Figure 3 is a map of the study area in relation to Gainesville and Alachua County within the state of Florida, and Figure 4 shows the relationship of study location with the surrounding landscape.

The site was determined to be nearly level, by topographical survey, with a slope to the south of less than 60 cm fall in 1.5 kilometers. A drainage ditch on the eastern side of the plantation effectively altered the natural drainage pattern. Water table wells located on the site demonstrated greater depth to water, throughout the experimental period, on the eastern flank of the experimental area. Records held by the landowners (Owens-Illinois Incorporated) show that no fertilization of the native or planted stand had taken place.

Site Description

Climate

Gainesville has a sub-tropical climate with a mean annual temperature close to 21°C (Bradley, 1972). The mean temperatures for the

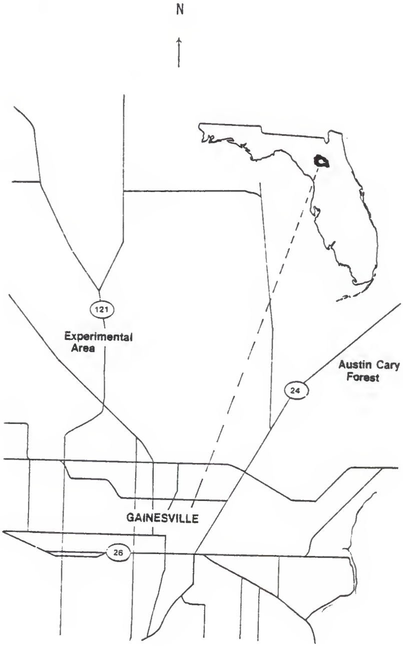

Figure 3. Location of experimental area in relation to Gainesville and Alachua County, Florida.

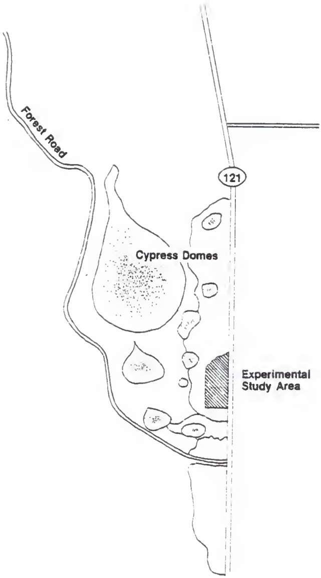

Figure 4. Location of study area in relation to other features of the landscape.

hottest month (July) are 33°C maximum and 22°C minimum; the corresponding temperatures in the coldest month (January) are 21.5°C and 12°C. Mean annual soil temperature at 50 cm is 23°C (hyperthermic).

Mean annual precipitation for the 47 years, 1930-1977, was 1337 mm (Prine, 1978). About half of the annual rainfall occurs in the summer months, June through September. More importantly, however, is the fact that this rain occurs in a pattern of thunderstorms and many stations average more than 80 thunderstorms per year (Bradley, 1972). Such thunderstorms are often heavy and last usually 1 to 2 hours, occurring during the hottest part of the day. Heavy rain showers occur at most places on about half of the summer days (Butson and Prine, 1968), and excessive leaching of sandy soils coupled with waterlogging of poorly drained soils is a common occurrence. Prolonged periods of deficient rainfall, nevertheless, are occasionally experienced even in the summer months.

Rainfall for the year 1978 recorded at the University of Florida Agronomy Farm weather station was 1857 mm. Monthly gaugings for this station and monthly throughfall data recorded at the experimental location for the year commencing July 1978 are shown in Figures 5 and 6. The pattern of throughfall on the experimental area followed that of rainfall recorded at the Agronomy Farm, but was generally less in magnitude.

Soils

The experimental area was located on a Pomona-Wauchula fine sand association classified as an Ultic Haplaquod, sandy, siliceous, hyperthermic (Carlisle et al., 1978).

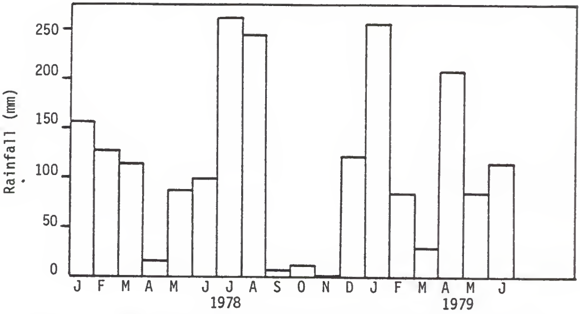

Figure 5. Monthly rainfall data for 1978-79 from University of Florida weather station.

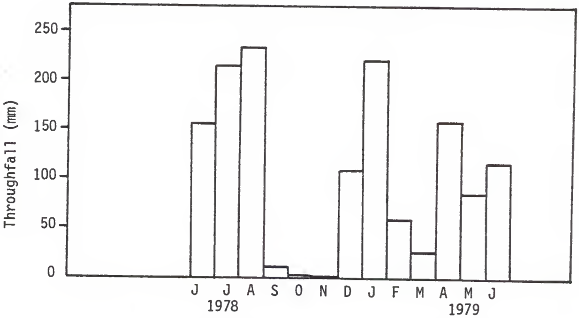

Figure 6. Monthly throughfall data for 1978-79 from the experiment location.

This somewhat poorly drained soil complex was typified by rapid permeability in the surface horizons and moderate permeability in the spodic and argillic horizons. A detailed soil profile description is found in Appendix Table 34.

Basic physical and chemical properties of surface mineral horizons prior to treatment (Table 3) showed the soil to be acidic in all horizons with the A2 horizon slightly less so. All horizons had a very high percentage of sand with small amounts of silt and clay. Bulk density increased with depth to the A2 and decreased again in the spodic horizon. Cation exchange capacity (CEC) was very low by agricultural standards, the A2 horizon had almost a tenfold decrease from the A1 horizon, and the spodic horizon showed an increase in CEC compared with the A1. Organic matter data showed a similar trend to that of the CEC.

The typical dependence of CEC on soil organic matter in sandy Spodosols in shown in Figure 7. Analysis for extractable elements has shown phosphorus to be high compared with other data for a Wauchula fine sand (Burger, 1979). It was suggested by *Pritchett (1979) that this could indicate proximity to phosphate rich limestone parent material. Extractable element concentrations are characteristic of the Spodosols in the region, high extractable Al in the spodic horizon, and low content for all elements in the A2 horizon.

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*Note: Personal communication.

Table 3. Physical and chemical properties of Wauchula fine sand, from the experimental location.

Horizon	FF[5]	A1	A2	B2h
Depth (cm)	10	11	27	*8
Total sand (%)	--	92.7	92.8	87.7
Silt (%)	--	4.8	5.4	5.4
Clay (%)	--	2.5	1.8	6.9
Bulk density (g/cc)	--	1.25	1.53	1.43
pH[1]	4.0	4.0	4.5	4.2
CEC (meq 100 g)[2]	--	3.42	0.39	5.81
Organic matter (%)	--	2.14	0.37	3.59
Total N[3] (%)	0.85	0.04	0.009 572	0.05 572
C:N ratio	--	31:1	24:1	42:1
Extractable elements[4]				
Al (ppm)		51.0	13.1	67.0
Ca (ppm)		100.0	26.0	31.0
Mg (ppm)		21.0	5.1	5.0
K (ppm)		10.3	2.9	5.9
Na (ppm)		13.2	8.7	12.3
P (ppm)		2.0	0.8	13.3

*Only 8 cm of the B2h was sampled.

[1] pH was determined on 1:2 soil:water suspension.

[2] CEC was by NH_4OAc buffered to pH 4.1.

[3] Total N by micro-Kjeldahl (Nelson and Sommers, 1972).

[4] Double acid extractable (Mehlich, 1952).

[5] FF = forest floor.

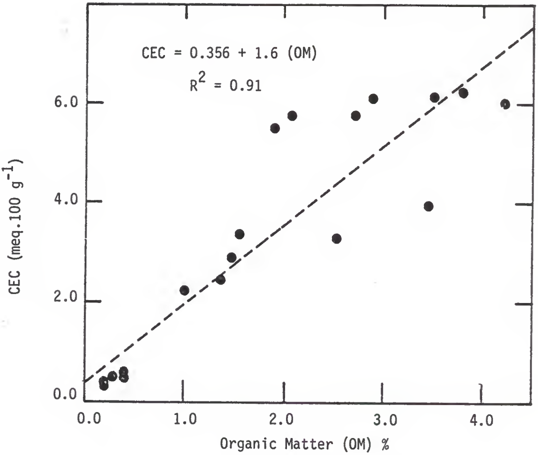

Figure 7 . Relationship between soil organic matter % and cation exchange capacity (CEC), for three mineral horizons of Wauchula fine sand.

Vegetation

This site was initially selected following a reconnaissance soil survey to establish the degree of uniformity in soil characteristics.

A representative of the landowners indicated that the area was managed for naval stores production prior to being cleared and planted to slash pine, utilizing minimum site preparations techniques, in 1955-56. The pines were planted east-west at approximately 2000 stems ha^{-1}, using 2.5 m row spacing and 2 m between trees within rows. The stand was well-stocked but with some areas of localized mortality and suppression. Fusiform rust (*Cronartium fusiforme*) infected a small percentage of trees.

Understory vegetation consisted of saw palmetto (*Serenoa repens* (B.) Small), wiregrass (*Aristida stricta* Michx.), runner-oak (*Quercus minima* (Sarg.) Small), gallberry (*Ilex glabra* (L.) Gray), and occasional regenerating saplings of long leaf pine (*Pinus palustris* Mill.), wax myrtle (*Myrica cerifera* L.), red-bay (*Persea borbonia* (L.) Spreng), huckleberry (*Gaylussacia frondosa* L., T., and G.), blueberry (*Vaccinium myrsinites* Lam.), and in open areas, some grasses (*Panicum* spp.) together with other forbs.

Field Experiment #1

Design and Installation

This was the main field experiment and was installed on June 27th, 1978, to monitor the fate of N fertilizers applied to a flatwoods forest. Volatile losses of ammonia and the vertical distribution of N and other elements were measured periodically for 128 days.

A randomized block design, with three blocks of ten treatment plots, was employed (Figure 8). Each treatment plot consisted of an area 10 m x 5 m encompassing three rows of pine trees (Figure 9). The treatments were factorial combinations of two N sources, urea and ammonium sulfate at levels 0, 100, 200, 300, 400 kg $N \cdot ha^{-1}$.

Uniform application for the study was achieved by spraying the fertilizer onto the forest floor in a water solution. Fertilizer applied by spray was confined to four 1 m^{-2} subplots located one in each quadrant of the treatment plot (Figure 9). The remaining plot area was treated with solid fertilizer broadcast with a cyclone-type seeder. Allowance was made for overspray and overspread in fertilizer quantities applied by each method. Tests were carried out to measure the degree of uniformity and the amount of fertilizer N applied.

Soil Sampling

Soil samples were collected 2 months prior to the fertilizer application in order to characterize the soil. In addition, a sampling was made four days before the fertilization and 2, 4, 8, 12, 16, 21, 32, 64, and 128 days after the plots were treated.

Soil samples were taken using a steel tube 5 cm in diameter. The sampling tube was manually driven into the soil until the spodic horizon had been penetrated at least 8 cm. The soil core taken in this fashion was inspected on the open face of the sampling tube and debris collected in this face during withdrawal was removed. The soil core was then divided into horizon sections and the depth of each horizon was measured whilst in the tube. Each soil horizon was placed

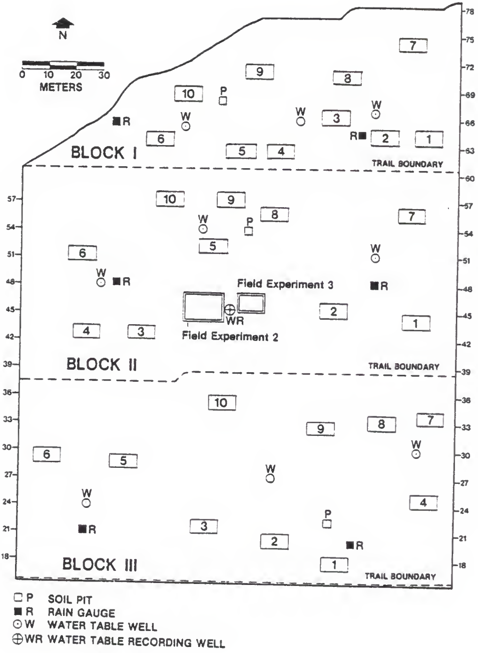

Figure 8. Field experiment #1, design and layout, also the location of field experiments #2 and #3 within the main area.

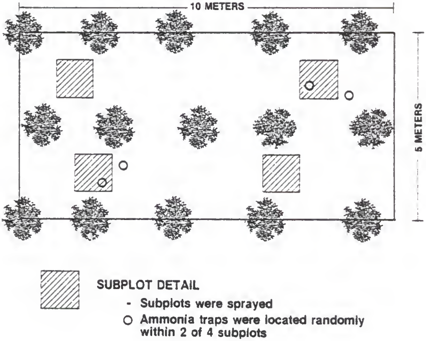
10 METERS
5 METERS
SUBPLOT DETAIL
- Subplots were sprayed
○ Ammonia traps were located randomly within 2 of 4 subplots

Figure 9. Location of subplots within the treatment plots and the positioning of ammonia traps within and adjacent to the sprayed subplots.

into a separate plastic bucket. Four such cores, one from each sprayed subplot, were bulked, thoroughly mixed, subsampled, labelled, and sealed in polyethylene bags. Sealed soil samples were placed in a portable cooler, transported to the laboratory and held in a freezer at -10°C until ready for chemical analysis.

Bulk densities were determined on soil samples collected from the major horizons from a soil pit located in each experimental block (Table 3). A bulk density sampler was used to take five replicate cores from each soil horizon chosen from different places around the soil pit. Bulk density cores were sealed in cans and dried at 105°C to a constant weight. Bulk density was characterized at two different times during the course of the project: April 1978 (Spring) and December 1978 (Winter).

Ammonia Sampling

Ammonia volatilization losses were estimated for each fertilizer and rate combination. Four gas traps, constructed from 4.2 cm PVC tubing 20 cm in length sharpened at one end and sealed at the other with a rubber stopper, were located in each of the 30 treatment plots. Within each treatment plot two of the sprayed subplots were selected at random and two of the four gas traps were located one on each of these subplots. The remaining two gas traps for each plot were located on solid application areas, but were paired with the gas traps already located on the sprayed subplots. This resulted in two pairs of gas traps per treatment plot.

The gas traps were driven lightly but firmly through the litter layers, and a glass microfiber filter paper, previously treated with a 4% boric acid solution, was attached to the underside of each rubber stopper. The glass filters were collected on the same days that soil samples were taken, sealed in glass vials and refrigerated until analyzed. Figure 10 shows the details of ammonia traps construction.

At each sampling time the gas graps were physically relocated within the same subplot and plot in order to reasonably account for the effects of rain between sampling dates.

Field Experiment #2

This experiment was installed on the 8th of April 1979 to characterize short term denitrification from the fertilizer sources used in field experiment #1 at a time thought favorable for the denitrification process. This was a completely randomized design with three replications in which treatments were combinations of urea or ammonium sulfate at levels of 0, 200, and 400 kg $N.ha^{-1}$. Plots were only 1 m^2 in area and treatments were applied by spraying the fertilizer onto the plots. Immediately following fertilization additional water at a rate of 0.5 cm was sprayed over the whole plot area. This was done to wash fertilizers well into the soil surface in order to reduce ammonia volatilization in an experiment designed to measure N_2O losses.

Gas traps to monitor evolution of N_2O were installed following treatment application. Each trap consisted of thick-walled 25 cm diameter PVC pipe driven 10 cm into the ground and standing 10 cm

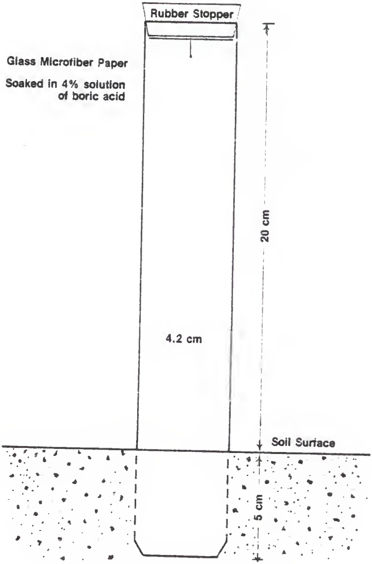

Figure 10. Details of static ammonia traps.

above the ground. Two access tubes were fitted to each trap to allow simultaneous sampling of the soil atmosphere below the entrapped soil surface. The traps were sealed above ground with a latex rubber ring and plexiglass lid to which had been fitted two serum stoppers (Figure 11). These traps remained on the treatment plots of field experiment #2 undisturbed following fertilization. In order to estimate denitrification losses at any point in time, traps were closed for the minimum time necessary to generate a readily detectable difference in N_2O concentration between inside and outside the traps, usually one hour. Duplicate samples were drawn from the head space and from the soil atmosphere on a sequence of days following fertilization. Gas samples were taken using 1 ml plastic syringes, each syringe first having been flushed with sample gas at least 6 times. Samples were sealed with rubber stoppers for transport to the laboratory.

Field Experiment #3

This experiment was installed on May 1, 1979, 23 days after experiment #2, to investigate potential denitrification losses from 3 N fertilizers. This experiment employed a completely randomized design with 2 replications of urea, ammonium sulfate, and ammonium nitrate applied at 0 and 200 kg $N.ha^{-1}$. Treatments were sprayed onto 1 m^2 plots as in experiment #2. This experiment was installed adjacent to field experiment #2 (Figure 8). Rainfall and throughfall data were collected for the duration of these latter 2 experiments, and

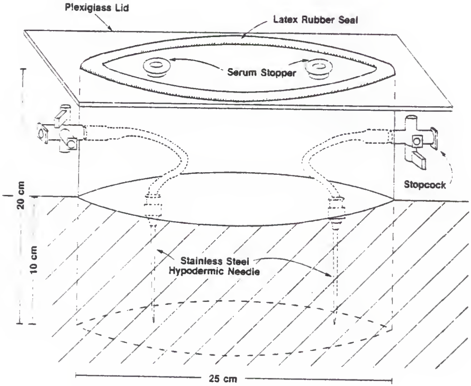

Figure 11. Construction details for static traps used to measure N_2O fluxes from the soil.

gas sampling was designed around and between significant rainfall events in order to investigate the relationships between precipitation and denitrification.

Laboratory Procedures

Soil Extraction

Two tests were conducted to ascertain the best extraction solution to meet the objectives of the study. These tests investigated the effect of the microbial inhibitor phenylmercuric acetate on subsequent total soluble carbon analyses performed on the soil extract. They also compared salt solutions with deionized water for the recovery of added urea, coupled with various methods of extraction.

Soil extraction test #1

The aim of this experiment was to compare N KCl, 2 N KCl, 0.01 M $CaCl_2$, and deionized water as extracting solutions for urea applied to a forest soil. Three different methods of extraction were combined into a factorial experiment with the solutions and replicated four times. Extraction methods one and two involved leaching of soil cores with a technique used by Stanford and Smith (1972), the third method involved shaking the soil and extracting solution as used by Douglas and Bremner (1970). The soil used for this test was a Wauchula fine sand collected from another similar forest site. Soil samples were taken by driving a sharpened 4.5 cm diameter PVC tube into the soil to a depth of 15 cm, and leaving the soil core sealed into the

PVC tube. For the first extraction method samples were left in the PVC tube without any further disturbance. Samples for the second method were removed from the tube, mixed, and put back into the PVC tube and sealed. For the third method soil samples were removed from the PVC tube, mixed, subsampled, and 10 g of soil placed into extraction jars.

Urea at the rate of 50 $\mu g.g^{-1}$ soil was added in solution to cores and extraction jars, immediately followed by addition of the microbial inhibitor phenylmercuric acetate (PMA) at the rate of 50 $\mu g.g^{-1}$ soil. Each soil column was leached with 400 ml of extracting solution under a tension of one atmosphere five minutes after urea addition. One hundred milliliters of extraction solution were added to the jars, and they were shaken for 1 hr on a horizontal shaker. These soil suspensions were filtered with a 0.2 micron millipore filter assembly. Column leachates and filtrates were analyzed for urea using the methods of Douglas and Bremner (1970).

Results were expressed as percentage (%) recovery of urea (Table 4). Analysis of variance of these results showed that there were no significant differences in the amounts of urea extracted by the four extraction solutions employed. Shaking the soil suspension for one hour and leaching mixed soil in columns recovered significantly more urea than leaching undisturbed soil in columns.

Water extracts from all methods were more highly colored than salt extracts indicating the presence of more dissolved C in the water extracts. Since one of the objectives is to attempt to relate N movement with dissolved C and elemental cations, it was decided to use deionized water and the shaking method. The results of

Table 4. Mean percentage recovery of added urea.

Extraction Method	Extraction Solution	Mean Recovery
Shaking for one hour	water	93.6%
	0.01 m $CaCl_2$	98.6
	N KCl	97.4
	2 N KCl	101.0
Leaching mixed soil cores	water	98.6%
	0.01 M $CaCl_2$	92.0
	N KCl	97.6
	2 N KCl	93.8
Leaching undisturbed soil cores	water	85.0%
	0.01 M $CaCl_2$	87.0
	N KCl	87.8
	2 N KCl	93.8

Extraction Method	Mean Recovery (%)
Shaking	97.6^{a*}
Leaching (mixed soil)	95.4^{a}
Leaching (undisturbed soil)	88.4^{b}

Extraction Solution	Mean Recovery (%)
2 N KCl	96.2^{a}
N KCl	94.2^{a}
0.01 M $CaCl_2$	92.6^{a}
water	92.4^{a}

*Means followed by the same subscript are not significantly different at the 95% level using Duncan's Multiple Range procedure.

test #1 indicated that the use of deionized water and shaking gave a good recovery of urea.

Phenylmercuric acetate effectively inhibited the hydrolysis of urea in this experiment, but did interfere with extractable carbon analyses if it was greater than 10 ppm in water.

Soil extraction test #2

This test was conducted to compare deionized water and N KCl as extractants of ammonium (NH_4^+) from Wauchula fine sand.

Simultaneous extractions using deionized water and N KCl were performed on a selection of routinely collected soil samples from the major installation.

Results of this experiment indicated that at the NH_4^+ levels encountered in the unfertilized soil, water gave similar results to N KCl, but when fertilized soil was extracted, N KCl gave significantly higher recoveries of NH_4^+ from both ammonium sulfate and urea treated soil.

Regressions were calculated for water and N KCl recovery of NH_4^+ from ammonium sulfate and urea treated A1 soil. These regressions can be expressed as follows:

(a) if soil has been treated with ammonium sulfate, NH_4^+ (H_2O recoverable) = -0.293 + 0.679 NH_4^+ (N KCl recoverable),

(b) if soil has been treated with urea, NH_4^+ (H_2O recoverable) = 1.20 + 0.072 NH_4^+ (N KCl recoverable). All NH_4^+ is measured in ppm oven dry weight (ODW) of soil.

*Rao (1979) suggested that the coefficients for these regressions

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*Note: Personal communication.

would be an expression of the relationship between the exchangeable and adsorbed NH_4^+ in this system.

Soil Analysis

The soil samples taken 2 months prior to treatment application were used to provide background physical and chemical characterization data for the experimental site. These samples were air-dried, sieved to pass a 2 mm mesh, and analyzed for pH and certain mineral elements which included Al, Ca, Fe, K, Mg, Na, and P.

Soil pH was determined on a 2:1 water:soil suspension using a pH-sensitive glass membrane electrode. Cations listed above were determined using atomic absorption (Al, Ca, Fe, Mg) and flame emission (K, Na) spectrometry. Phosphorus was determined colorimetrically using a *Technicon Auto-Analyzer.

Soil organic carbon was determined by the modified Walkley-Black method (Jackson, 1958) for all initial samples. Cation exchange capacity was determined by ammonium saturation using normal ammonium acetate at pH 4.1 (Chapman, 1965) on samples prepared by subsampling and bulking material from each horizon separately for five adjacent plots in each block, resulting in a total of 18 samples of each soil mineral horizon.

Particle size distribution was determined by the hydrometer method (Day, 1965), with additional separation of the sand fraction by dry sieving for 15 minutes using U.S. standard sieves. The results of

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*Note: Technicon Industrial Systems, Tarrytown, N.Y.

this early sampling make up the major part of the characterization data presented in Table 3.

Samples collected from field experiment #1 and stored at -10°C were allowed to thaw in a refrigerator at 2°C. A moist 20 g subsample of the previously bulked sample was shaken for one hour with 100 ml of deionized water to which had been added phenylmercuric acetate at the rate of 10 $mg.l^{-1}$. A second subsample of 10 g was taken to determine moisture content. The soil suspensions were filtered using a 0.20 micron millipore filter unit and refrigerated.

All litter ODW determinations were corrected for sand impurities by sieving the O.D. litter samples, collecting the sand and fine organic matter which passed through the sieve, then ashing the sandy sample. The ashed weight of sand is subtracted from litter ODW to correct for unreactive sand content.

Total N in all soil samples was determined by the tube digestion method (Nelson and Sommers, 1972) with steam distillation and back titration (Bremner, 1965b) to determine NH_4^+ in the digest. A similar procedure (Nelson and Sommers, 1975) was used to determine total N in the soil extract; since extract nitrite + nitrate (NO_2^- + NO_3^-) concentration was always less than 0.5% of the extract total N concentration. No reduction step was undertaken in either procedure. Extract NH_4^+ and NO_2^- + NO_3^- were determined by steam distillation and back titration with dilute acid (Bremner, 1965b).

Urea nitrogen in the soil extract was determine colorimetrically by the method of Douglas and Bremner (1970). Total carbon (inorganic plus organic) determinations were made on all water extracts. This analysis was carried out on a *Beckman model 915A, Total Organic Carbon Analyzer, coupled with a *Beckman model 865 infrared analyzer.

Extract pH (5:1, water:soil) was determined using a glass-membrane electrode. Cations and P were determined on each soil extract by the procedures mentioned above for the site characterization.

Ammonia Volatilization Analysis

Ammonia which was trapped on the boric acid treated filter papers was determined by alkaline steam distillation using MgO and procedures outlined by Bremner (1965b). The distillate was back titrated using 0.005 N H_2SO_4 in a microburette.

Nitrous Oxide Analysis

Nitrous oxide gas samples were injected into a **Tracor model 222 gas chromatograph fitted with a nickel-63 high temperature electron capture detector. Routine operational temperature for this detector was 365°C. Oven temperature was maintained isothermally at 45°C following a conditioning period at 150°C. The carrier gas was a 95:5 ratio mixture of argon and methane, flowing at a rate of 20 ml. min^{-1} by maintaining a pressure of 3.51 $kg.cm^{-2}$ (50 $lb.in^{-2}$). The electrometer was equipped to maintain a D.C. potential across the nickel-63 foil within the detector. Gas samples passed through a stainless

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*Note: Beckman Instruments, Inc., Fullerton, California.

**Note: Tracor Inc., Austin, Texas.

steel column 4 m long packed with 100-120 mesh porapak Q. Nitrous oxide retention time was just under 4 minutes and N_2O was quantified by recording peak height response on a strip chart recorder and comparing sample peak height with the calibration line for primary standard N_2O each time samples were analyzed. Peak height was linear in the range 0.1-4.0 ppm of N_2O.

Carrier gas flow was maintained continuously in order to minimize contamination of the detector from the air inside the laboratory.

RESULTS

Ammonia Volatilization

Highly significant differences in NH_3 trapped daily were recorded for urea and ammonium sulfate applications. In addition there were significant effects due to rate and mode of application. Amounts of NH_3 volatilized from urea treatments were higher than the amounts trapped from plots fertilized with ammonium sulfate for all periods until day 64. Ammonia trapped during the period from 64 to 128 days after treatment was not different between fertilizers (Table 5; Figure 12).

Analysis of methods of application revealed that on day 2, NH_3 trapped from sprayed subplots was significantly greater than that trapped from solid fertilizer applications (Figure 13). From day 4 through day 64 solid applications resulted in significantly more volatilization of NH_3.

Cumulative amounts of NH_3 volatilized (Figure 14) for the 128 day observation were analyzed separately and mean cumulative NH_3 volatilized for 128 days (Table 6) revealed that urea applied at 300 kg $N \cdot ha^{-1}$ resulted in the highest gaseous NH_3 loss (8.99 kg $NH_3\text{-}N \cdot ha^{-1}$). There was no significant difference between urea applied at 100 kg $N \cdot ha^{-1}$, ammonium sulfate at all rates, and control measurements of NH_3 volatilized.

Table 5. Average NH_3 volatilization from urea and ammonium sulfate fertilized plots, for 128 days following application of liquid or solid fertilizer.

Time	Fertilizer		Application method	
Sampling day	Urea	Ammonium sulfate	Solid	Spray
	$kg\ NH_3\text{-}N \cdot ha^{-1} \cdot d^{-1}$			
2	0.735^{a}[1]	0.046^{b}	0.080^{b}	0.725^{a}
4	0.993^{a}	0.017^{b}	0.520^{a}	0.520^{a}
8	1.031^{a}	0.024^{b}	0.638^{a}	0.462^{b}
12	0.94^{a}	0.010^{b}	0.484^{a}	0.511^{a}
16	0.382^{a}	0.016^{b}	0.284^{a}	0.134^{b}
32	0.097^{a}	0.028^{b}	0.021^{a}	0.055^{b}
64	0.021^{a}	0.017^{b}	0.021^{a}	0.018^{b}
128	0.033^{a}	0.032^{a}	0.032^{a}	0.032^{a}

[1] Means with the same letter are not significantly different at the 95% probability level, using Duncan's multiple range test.

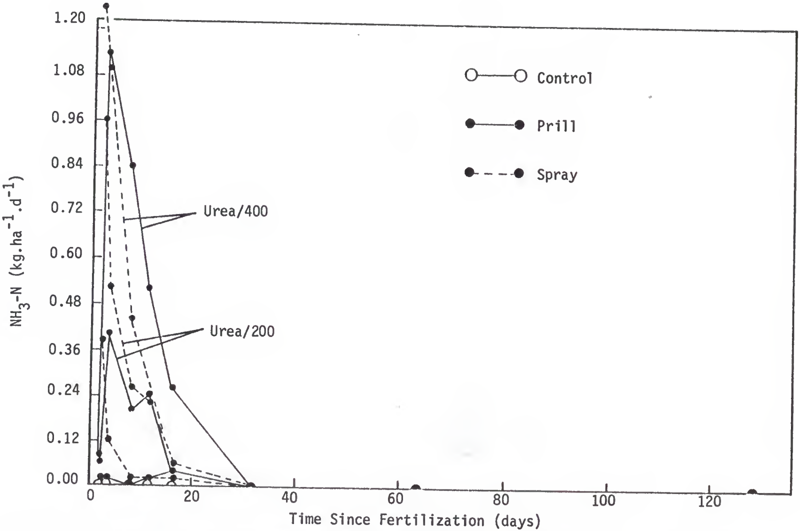

Figure 12 . Volatilization of ammonia (NH_3) during 128 days following fertilization with urea.

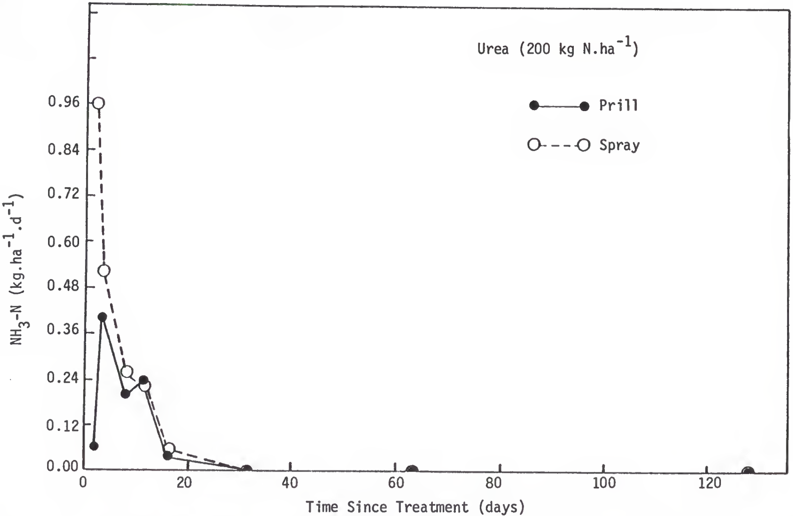

Figure 13. Effect of method of application of 200 kg urea-N.ha^{-1} on initial daily volatilization of NH_3.

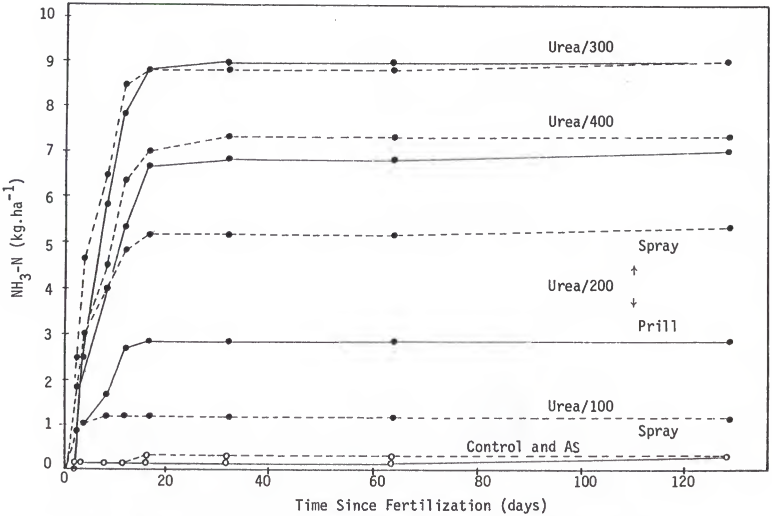

Figure 14. Cumulative volatile loss of NH$_3$ during 128 days following fertilization.

Table 6 . Cumulative NH_3 volatilized during 128 days following fertilization.

Treatment		Ammonia loss
Fertilizer source	Rate of application (kg N·ha^{-1})	Mean cumulative NH_3 volatilized for 128 days (kg NH_3-N·ha^{-1})
Nil	0	0.10^{c}[1]
Ammonium sulfate	100	0.16^{c}
	200	0.13^{c}
	300	0.35^{c}
	400	0.29^{c}
Urea	100	0.81^{c}
	200	4.08^{b}
	300	8.99^{a}
	400	7.15^{a}

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[1] Means with the same letter are not significantly different at the 95% probability level, using Duncan's multiple range test.

Rainfall and Ammonia Volatilization

The first significant rainfall recorded occurred 10 days after fertilization, and was the principal reason for the sampling carried out on day 12. Reduced NH_3 volatilization coincided with this initial rain storm and subsequent rainfall appeared to result in marked reduction in NH_3 measurements. However, the exponential decrease in mean daily volatilization also appeared to be a function of time since treatment. The natural logarithm of daily NH_3 volatilization was plotted as a function of cumulative throughfall (cum TF) (Figure 15; Table 7). The linear effect of cumulative throughfall explained 99% of the variation in the natural logarithmic transformation of daily NH_3 volatilization (DNV) expressed in g $NH_3\text{-N}\cdot\text{ha}^{-1}\cdot\text{d}^{-1}$, and can be represented by the following relationship: $\ln(\text{DNV}) = 5.53-0.014$ (cum TF) or

$$\text{DNV} = 5.53.e^{-0.014\ (\text{cum TF})}$$

where DNV = daily NH_3 volatilization ($\text{g}\cdot\text{ha}^{-1}\cdot\text{d}^{-1}$),

Cum TF = cumulative throughfall (mm).

A similar relationship was tested with time since fertilization as the independent variable. The resulting regression explained 98% of the variation in ln(DNV) if the data from day 128 are ignored for regression purposes (Figure 15). The ability of both time and cumulative rainfall to explain the exponential decline in NH_3 volatilization could be expected in this instance because time and cumulative throughfall also appear to be linearly related until 64 days after fertilization (Figure 16).

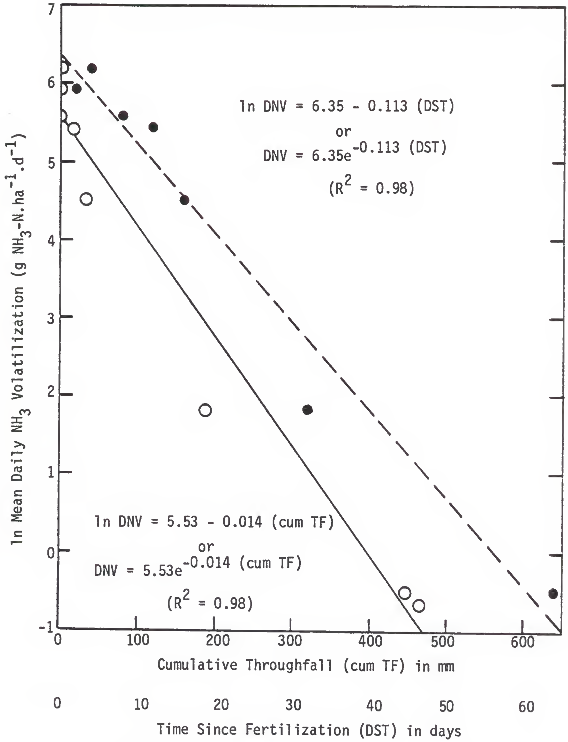

Figure 15. Relationship between the natural logarithm of NH_3 volatilization and cumulative throughfall or time.

Table 7. Cumulative throughfall (cum TF) and daily NH_3 volatilization (DNV).

Time since fertilization [DST] (days)	Mean daily NH_3 loss [DNV] ($g \cdot ha^{-1} \cdot d^{-1}$)	Natural logarithm [DNV] [ln(DNV)]	Cumulative rainfall [CUMRAIN] (mm)	Cumulative throughfall [CUMTF] (mm)
2	370	5.91	0	0
4	490	6.19	0	0
8	260	5.56	3.5	1.3
12	230	5.43	62	16.5
16	90	4.50	116	32.9
32	6	1.79	244	188
64	0.6	-0.51	471	449
128	0.5	-0.66	488	466

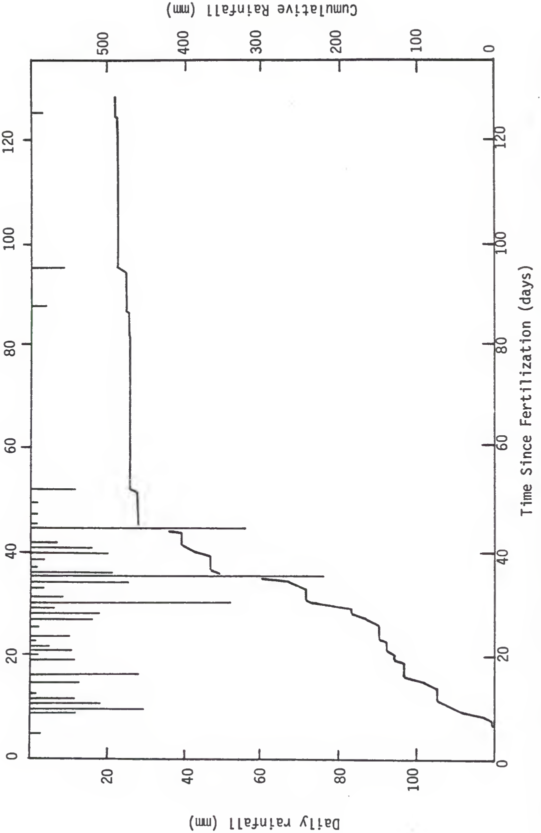

Figure 16 . Daily and cumulative rainfall measured at the University of Florida agronomy farm for 128 days following fertilization.

Soil Acidity

The mean of 30 pH determinations in 1:2 soil:water suspensions for each soil horizon averaged pH 4.0, 4.5, and 4.2 for the A1, A2, and B2h horizons, respectively (Table 3). Subsequently, pH was determined using a 1:5 soil to water suspension and fresh soil samples including the forest floor. Mean soil pH determined over all sampling times on control plots resulted in pH values of 4.1, 4.4, 4.8, and 4.5 for the forest floor, A1, A2, and B2h horizons, respectively.

A small study was conducted to correct these latter moist soil determinations to a 1:2 soil:water basis (Figure 17; Table 8).

Table 8 . Soil pH, for dry and moist soil samples corrected for 1:2 soil:water ratio.

Soil horizon	Air-dry soil	Moist soil	
	Soil:water ratio	Soil:water ratios	
	1:2	1:5	1:2
FF[1]	--	4.1	4.05
A1	4.0	4.4	4.2
A2	4.5	4.8	4.6
B2h	4.2	4.5	4.3

[1] FF = forest floor.

The 1:2 soil to water ratio resulted in a lower suspension pH value than the 1:5 ratio. Figure 17 indicates that 1:2 and 1:5 soil to water suspensions result in similar pH values for the forest floor

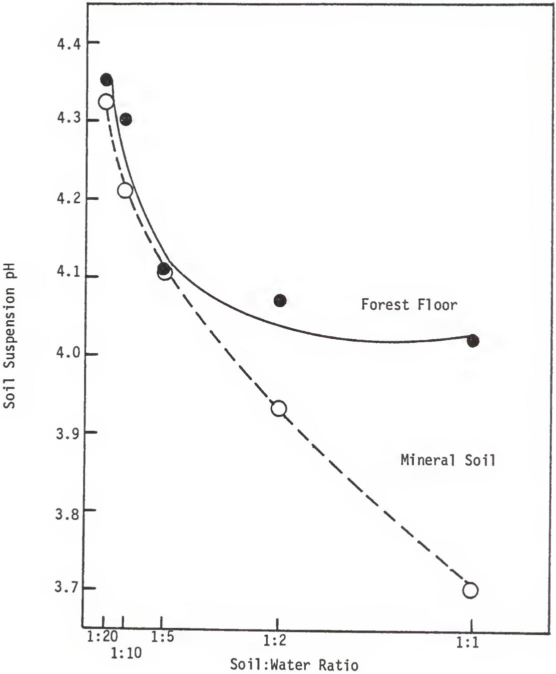

Figure 17. Changes in soil suspension pH with changes in the ratio of soil:water.

but that a 1:5 soil to water ratio for mineral soil results in a pH value almost 0.2 units higher than the 1:2 ratio. The difference of 0.1 pH units is unlikely to be critical for the purposes of this study.

Moist soil pH values were consistently 0.1-0.2 pH units higher than air dry soil values.

Change in pH (ΔpH) was determined for 1:2 air dry soil:solution, using water and normal potassium chloride (N KCl).

Soil pH determined in N KCl was less than pH in water (Table 9). The difference between pH in N KCl and water (ΔpH) indicated that the soil carried a net negative charge. The -ΔpH values also indicated that the soil pH was on the negative side of the zero point of charge. The pH values in the A2 and B2h horizons were less negative than in the forest floor, possibly indicating some positive surfaces in these soil horizons.

Table 9 . ΔpH values for Wauchula fine sand from the experimental location.

Soil horizon	pH in N KCl	pH in water	ΔpH	ΔpH - Blank[1] (0.34)
FF[2]	2.95	4.00	-1.05	-0.71
A1	3.06	4.00	-0.94	-0.60
A2	3.68	4.50	-0.82	-0.48
B2h	3.42	4.20	-0.78	-0.44

[1] Blank due to difference in pH between water and N KCl.

[2] FF = forest floor.

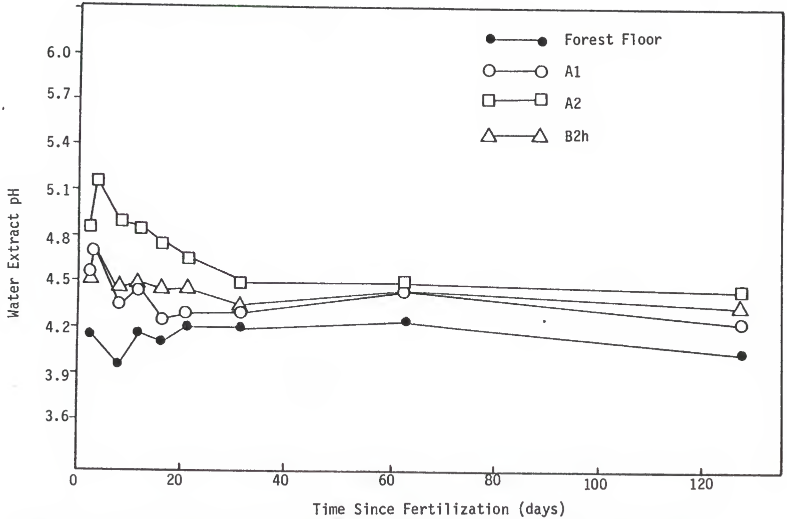

Figure 18. Soil extract pH in control plots during 128 days following fertilization.

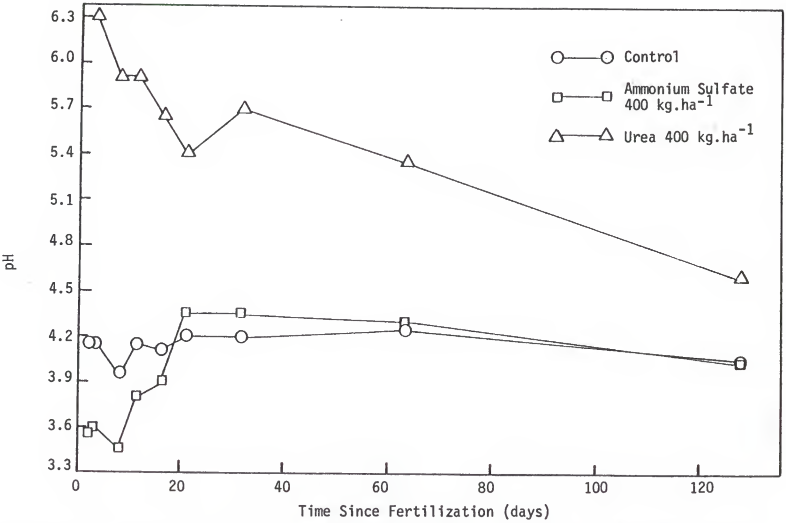

Figure 19. Changes in forest floor water extract pH during 128 days following fertilization.

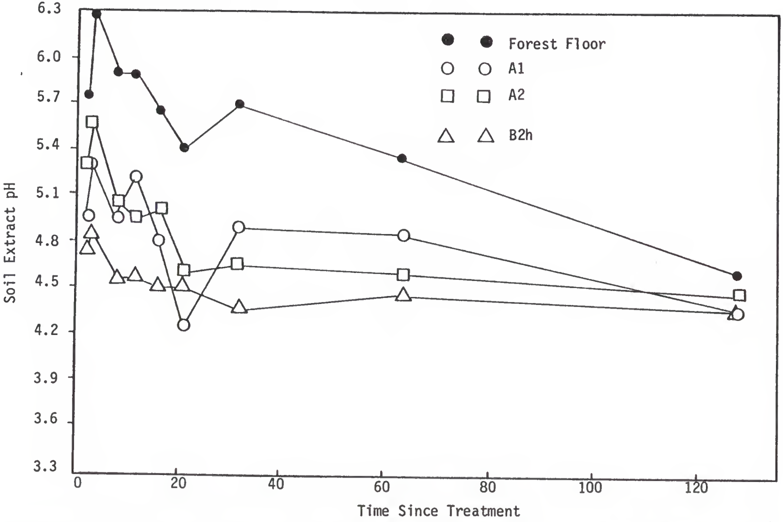

Figure 20. Soil extract pH during 128 days following fertilization with urea at 400 kg $N.ha^{-1}$.

Soil acidity measured on control plots (Treatment 1) showed that the highest pH was recorded in the A2 horizon throughout the experiment and that initially, differences in acidity between horizons was more marked than after 128 days (Figure 18). Early differences are shown in the mineral horizons especially, and might be attributed to renewed mineralization activity and release of organic acids in the forest floor. Later in the season, with almost no rainfall leaching of mineralization products could not take place.

Soil pH measured on 1:5 suspensions rose following urea treatments and was depressed initially following application of ammonium sulfate. The greatest pH changes were recorded in the forest floor extracts, associated with highest levels of fertilizer application (Figure 19). Intermediate increases of shorter duration were measured for the lower rates of fertilization, and for the mineral soil (Appendix Table 35; Figure 20). Elevated pH values remained for 128 days in the forest floor with high urea treatments, whereas depressed pH associated with ammonium sulfate persisted no more than 16 days (Figure 19).

Soil Total Nitrogen

Results of soil total N determined by micro-Kjeldahl procedures are listed in Appendix Table 36 for each soil profile horizon, treatment, and sampling time. Initial soil total N in control plots (Table 10) showed that the highest concentrations were in the forest floor, that the spodic (B2h) horizon had a greater concentration than the A1, and the A2 horizon had about one-quarter the concentration of soil total N as the A1. Soil total N in mineral horizons was not

Table 10. Variation in the concentration and contents of soil (STN) and soil extract total nitrogen (EXTN).

HOR	STN[1] (ppm)	STD[2] ERR	STN ($kg.ha^{-1}$)	STD ERR	EXTN (ppm)	STD ERR	EXTN ($kg.ha^{-1}$)	STD ERR
FF	8522	305	304	16	170	11	6	0.4
A1	358	18	541	32	9.3	0.5	13	0.7
A2	86	3.5	312	13	5.7	0.8	22	3.1
B2h	533	14	609	16	10	0.6	11	0.7

(Mean STN for the upper 50 cm of mineral soil plus forest floor at the experimental site was 1766 kg $N.ha^{-1}$, prior to treatment.)

[1] STN = Soil total N.

[2] STD ERR = Standard error of the mean.

altered very much with time (or season) but variation in soil total N for the forest floor was considerable (Figure 21). The rise in soil total N concentration to 10,500 ppm (ODW) of forest floor on day 64 following initial soil sampling was typical of the variation in soil total N determinations made on forest floor materials.

The effect of fertilization was readily seen in soil total N measurements in the forest floor following treatments (Figure 22). However, following initial heavy rains especially on days 10 and 16 after application the fertilizer additions were leached from the forest floor. Again, as with the control plots soil total N determinations show considerable variation, and from such determinations it would be difficult to resolve which source of N (urea or ammonium sulfate) was retained longer in the forest floor. Total N concentrations in the A1 and other horizons indicated a much reduced response to fertilization when plotted on the same scale (Figure 22). The data in Appendix Table 36 showed no discernable trend in soil total N determinations for each treatment, within mineral soil horizons. Total N in the forest floor on the experimental site expressed on an area basis was calculated by *Kushla (1978). He determined that the mass of forest floor was 35.7 tons$\cdot$ha^{-1}.

Total N in mineral horizons was calculated using horizon depth measured on each sampling day, and bulk densities listed in Table 3 . Horizon soil total N contents (Table 11 ; Figure 23) show that, prior to treatment the A1 and B2h horizons contained approximately twice as much N as the forest floor or A2 horizons. Total N to a

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*Note: Kushla, J., personal communication.

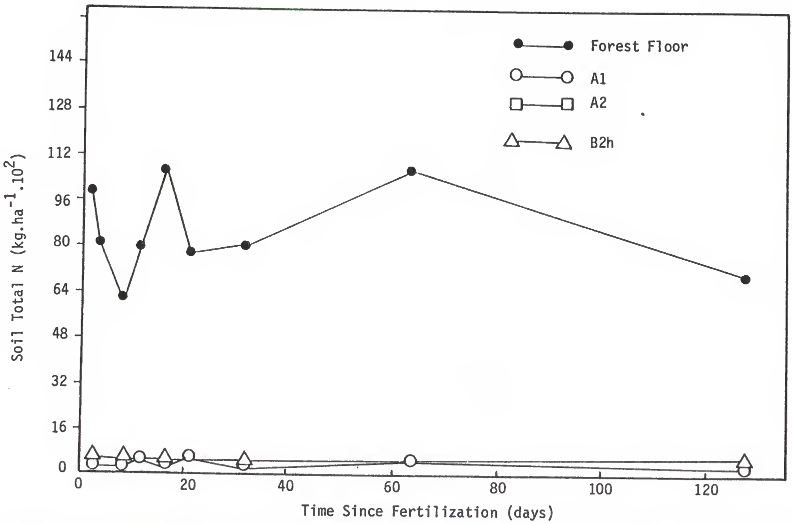

Figure 21. Distribution of soil total N in control plots during 128 days following fertilization.

Table 11 . Soil total nitrogen in the forest floor (FF) and spodic horizons (B2h) in control and N fertilized plots.

		Fertilizer source				
DST[1] (days)	Soil horizon	Nil	Ammonium sulfate		Urea	
		Rate of application (kg $N.ha^{-1}$)				
		0	200	400	200	400
		kg $N.ha^{-1}$				
0	FF	271	308	306	254	258
	B2h	630	544	418	673	606
2	FF	356	410	620	461	532
	B2h	709	510	486	704	664
4	FF	289	496	562	374	446
	B2h	554	582	513	704	647
8	FF	221	448	502	415	568
	B2h	618	475	575	636	552
16	FF	380	441	562	495	470
	B2h	596	551	624	810	716
64	FF	377	302	331	310	373
	B2h	588	552	646	704	702
128	FF	249	322	322	344	344
	B2h	733	523	547	668	600

[1] Days since treatment.

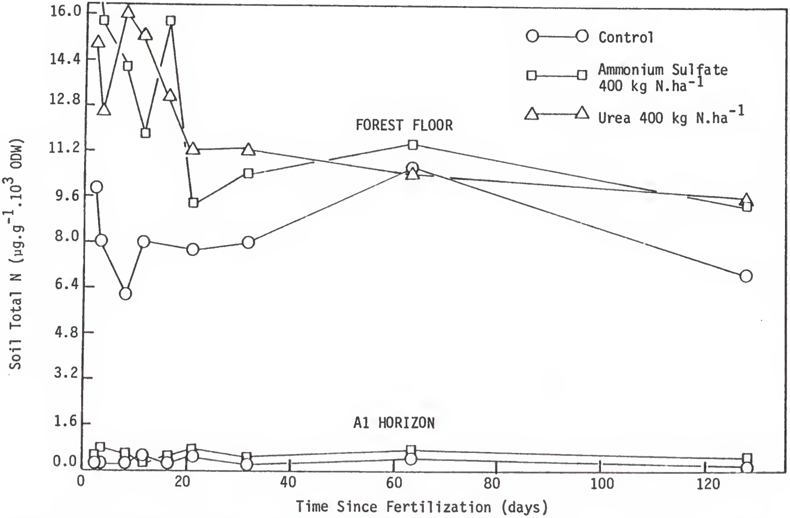

Figure 22 . Soil total nitrogen in the forest floor and A1 horizon during 128 days following fertilization.

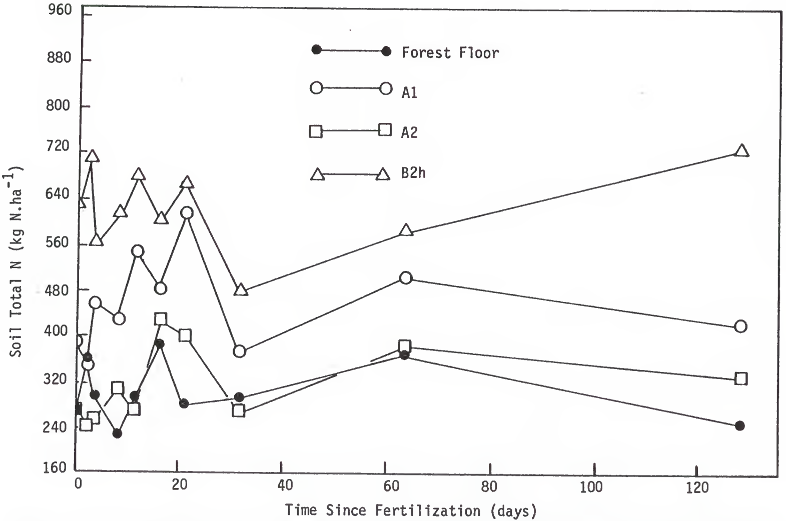

Figure 23. Distribution of soil total N in control plots during 128 days after fertilization.

depth of 50 cm amounted to 1760 $kg{\cdot}ha^{-1}$. By the eighth day following fertilizer application with ammonium sulfate at 400 kg $N{\cdot}ha^{-1}$ soil total N in the forest floor had fallen below that in the spodic horizon (Table 11). Urea applications of 200 and 400 kg $N{\cdot}ha^{-1}$ at no stage resulted in higher soil total N in the forest floor than in the spodic horizon. Applications of fertilizers did result in accretion of N in the A1 horizon; ammonium sulfate at 200 kg $N{\cdot}ha^{-1}$ influenced soil total N in the A1 for the whole sampling period. Ammonium sulfate applied at 400 kg $N{\cdot}ha^{-1}$ had a similar effect (Figures 24a and 24b), but the 200 kg application resulted in more soil total N in the A1 than did the 400 kg application. Applications of urea-N at high levels did not appear to differ markedly in their effect on soil total N from the ammonium sulfate treatments. Compare Figures 25, 24b, and 24a to see the effects on soil total N of fertilization at high levels.

Water Extractable Total Nitrogen

Water-extractable total N was most concentrated in forest floor extracts (Table 12), but the water-extractable total N was least from this horizon. Ammonium sulfate at 400 kg $N{\cdot}ha^{-1}$ resulted in marked increases in water-extractable total N, and equivalent levels of urea did not have the same initial impact on the forest floor (Figure 26). Water-extractable total N from mineral horizons was increased by fertilizer applications, but the influence of fertilizer on water-extractable total N was much reduced in the spodic horizon (Figures 27 and 28). Urea at 400 kg $N{\cdot}ha^{-1}$ and ammonium sulfate at 200

Table 12. Water-extractable total N during 128 days following fertilization.

DST[1]	Horizon	Fertilizer source				
		Nil	Ammonium sulfate		Urea	
		Rate of application (kg N.ha^{-1})				
		0	200	400	200	400
		kg N.ha^{-1}				
0	FF	6	6	9	5	6
2		9	118	386	46	83
4		6	112	223	30	97
8		5	89	179	39	79
16		6	54	73	31	49
64		3	4	5	8	8
128		2	4	3	5	8
0	A1	12	17	13	10	14
2		21	38	89	25	51
4		10	38	89	25	51
8		11	51	62	21	40
16		12	73	116	27	35
64		16	23	24	18	37
128		12	17	17	14	28
0	A2	19	14	18	18	14
2		27	57	85	51	88
4		13	41	55	23	28
8		18	43	46	32	33
16		23	59	97	35	27
64		68	43	37	48	74
128		29	41	49	11	8
0	B2h	10	10	9	11	12
2		19	17	22	20	24
4		11	14	14	18	16
8		12	7	8	16	12
16		10	9	9	11	9
64		15	17	45	25	19
128		13	12	19	18	10

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[1] Days since fertilization treatment.

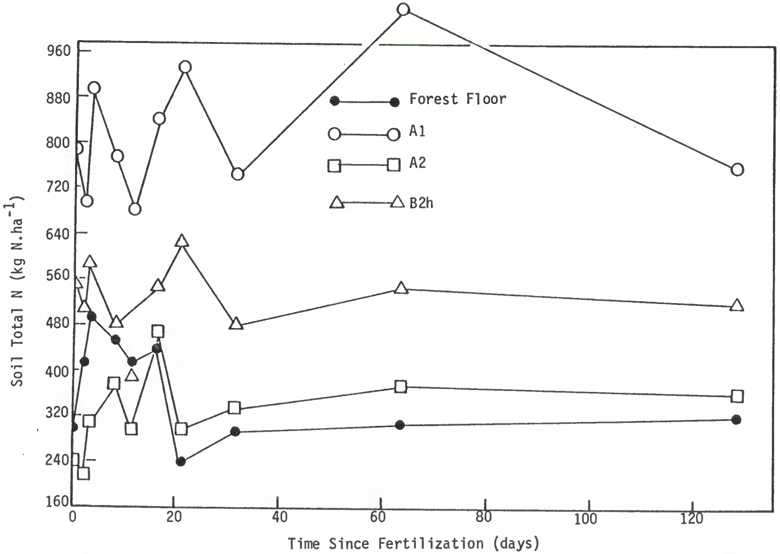

Figure 24a. Distribution of soil total N during 128 days following fertilization with ammonium sulfate at 200 kg N.ha^{-1}.

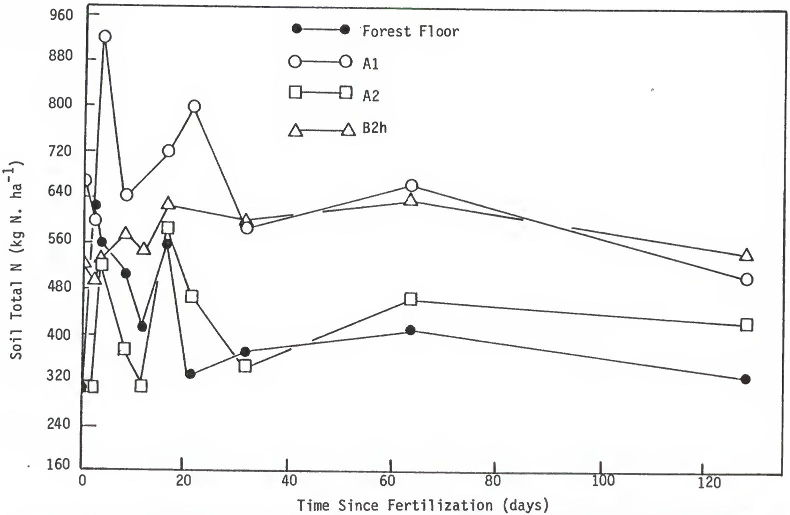

Figure 24b. Distribution of soil total N during 128 days following fertilization with ammonium sulfate at 400 kg N.ha^{-1}.

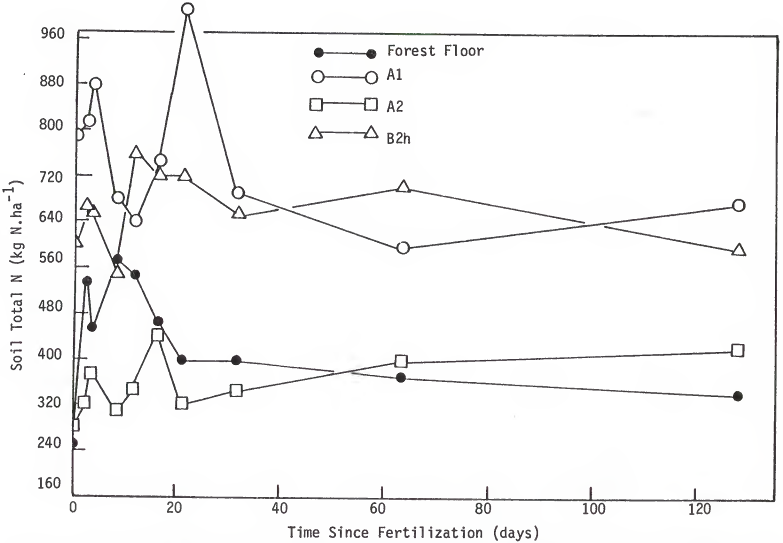

Figure 25. Distribution of soil total N, during 128 days following fertilization with urea at 400 kg N.ha^{-1}.

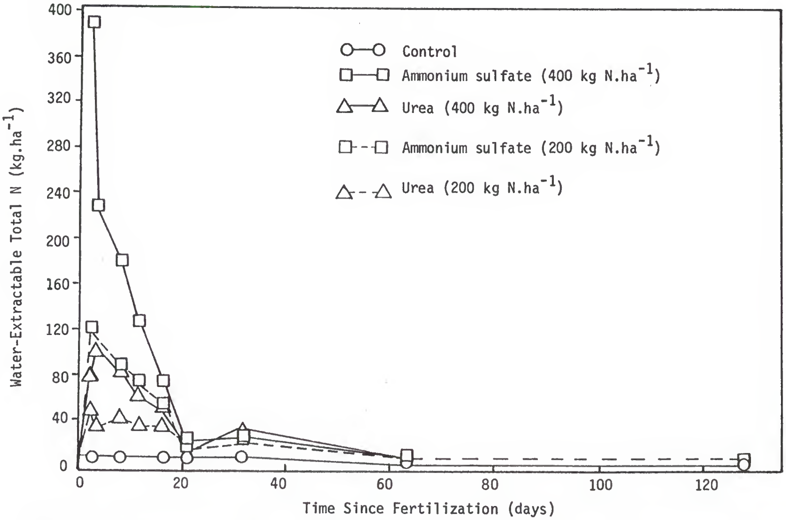

Figure 26. Water-extractable total N in the forest floor during 128 days following fertilization.

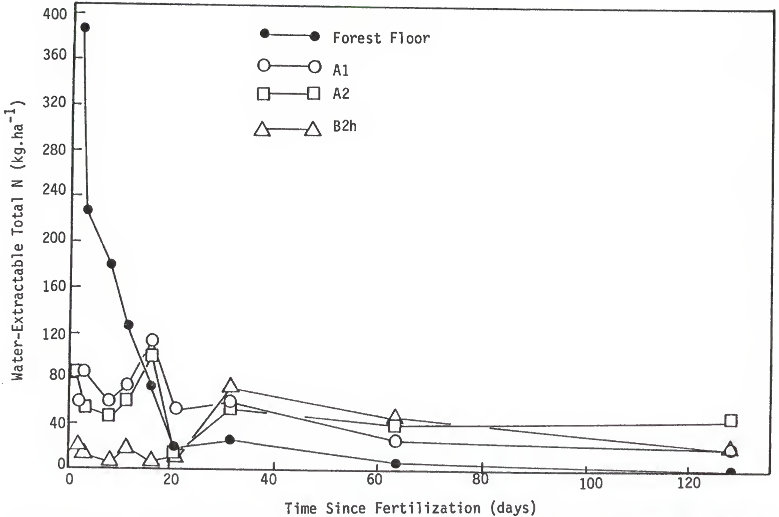

Figure 27 . Water-extractable total N for 128 days following fertilization with 400 kg N.ha^{-1} ammonium sulfate.

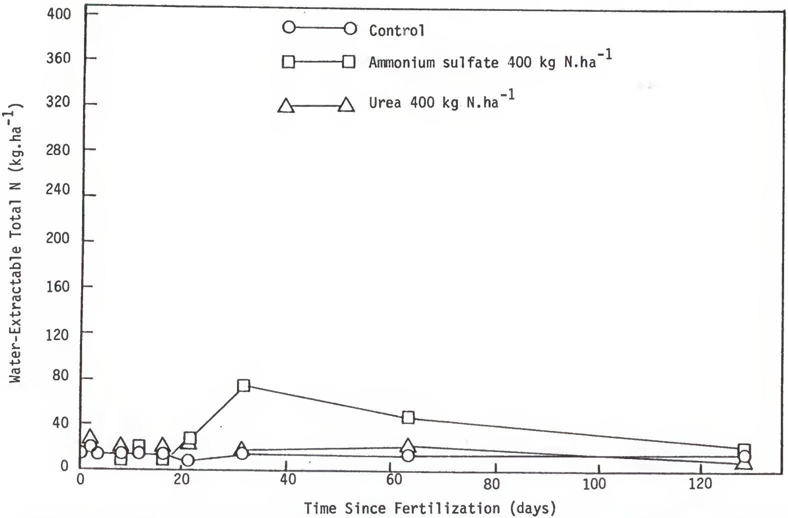

Figure 28 . Water-extractable total N from the spodic horizon, for 128 days following fertilization.

kg $N{\cdot}ha^{-1}$ appeared to result in similar levels of water-extractable total N, perhaps suggesting that 200 kg $N{\cdot}ha^{-1}$ from urea was not extractable by water (Figure 26). In the spodic horizon (B2h) water-extractable total N values showed a minimal response to fertilizer inputs indicating that soluble nitrogen did accumulate in this horizon and was not mobilized from this horizon to any appreciable extent. Even though the concentration was low in the A2 horizon, due to its depth this horizon contained as much water-extractable total N as the A1 horizon.

Ammonium (NH_4^+) Nitrogen

Water-extractable NH_4^+ was determined on all soil extracts; in addition KCl-extractable (using N KCl) NH_4^+ was calculated for each treatment combination using the regressions established from the results of soil extraction test #2.

When water was the extracting agent, the colloidal materials remained dispersed, especially for the urea treatments, but flocculation resulted when KCl was the extraction solution. However, these two extracting solutions brought into solution different phases of the NH_4^+; KCl extracted the exchangeable NH_4^+ whilst water removed only loosely absorbed NH_4^+ from soil particles. Consequently, less NH_4^+ was found in water extracts than in KCl extracts of the same sample. The results from these two extraction techniques are shown in Table 13.

The differences between water and N KCl extracting solutions are shown in Figures 29 and 30 . From Figure 29 it can be seen

Table 13. Ammonium content of water and N KCl extracts of the forest floor.

DST[1]	Nil	Ammonium sulfate		Urea	
	Application rate (kg $N.ha^{-1}$)				
	0	200	400	200	400
	Water-extractable NH_4^+				
	kg NH_4^+-$N.ha^{-1}$				
0	0.9	0.5	1.0	0.7	1.0
2	1.2	84	271	18	28
4	0.9	86	119	14	25
8	0.7	73	156	22	40
16	0.8	44	60	21	22
64	0.9	1	2	4	5
128	0.0	0.1	0.2	2	6
	KCl-extractable NH_4^+				
	kg $N.ha^{-1}$				
0	7	1	2	9	13
2	11	123	399	246	388
4	7	126	176	193	348
8	5	107	230	311	552
16	8	64	88	295	303
64	6	2	3	52	69
128	0.0	0.2	0.3	25	87

Fertilizer source: Nil, Ammonium sulfate, Urea.

[1] Days since fertilizer treatment.

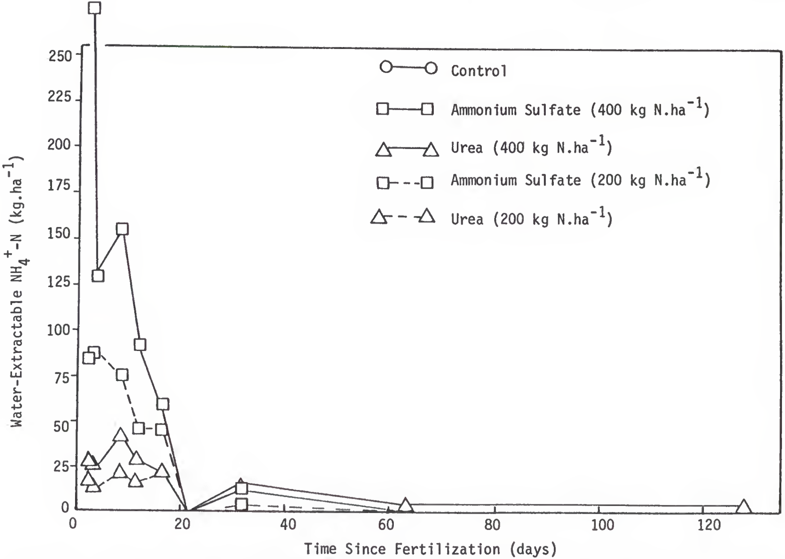

Figure 29. Water-extractable NH_4^+ in the forest floor during 128 days following fertilization.

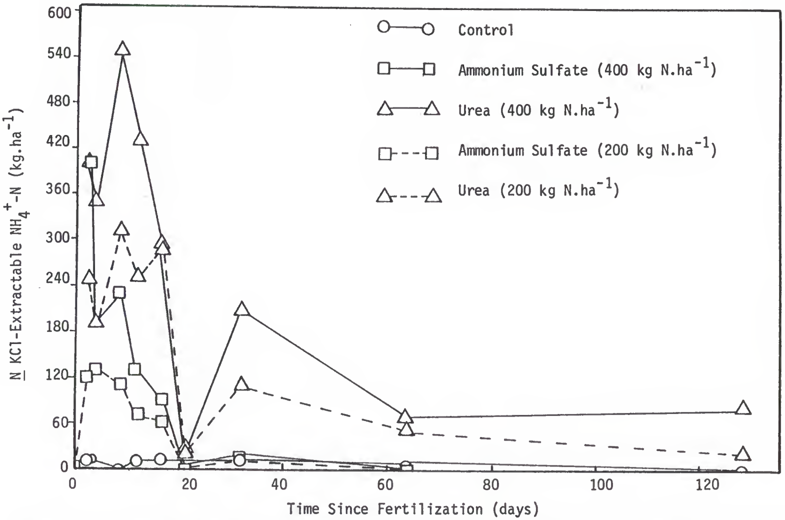

Figure 30. Normal KCl-extractable NH_4^+ in the forest floor during 128 days following fertilization.

that ammonium sulfate was more readily extracted with water than was urea, indicating that NH_4^+ arising from urea hydrolysis appeared to be more tightly bound to soil colloids than NH_4^+ from the dissociation of ammonium sulfate. It could alternatively mean that urea generates more exchange sites and, thus NH_4^+, is absorbed more firmly to the soil. The high levels of urea fertilization resulted in the persistence of exchangeable NH_4^+ (extracted by $\underline{N}$ KCl) in the forest floor; whereas, ammonium sulfate applications did not persist as long (Figure 30). Soil extractions 16 days after fertilizer application showed that NH_4^+ was leached from the forest floor and accumulated, mainly in the A1 mineral horizon immediately below the forest floor, following fertilization with ammonium sulfate at 400 kg $N \cdot ha^{-1}$ (Figure 31).

Urea fertilization at the highest rate resulted in increased levels of NH_4^+ in the A1 and A2 horizons following leaching rains. Potassium chloride extractable NH_4^+ from urea applied at 400 kg $N \cdot ha^{-1}$ on day 32 was determined to be 420 kg NH_4^+-$N \cdot ha^{-1}$ in the A1 horizon compared with 30 kg NH_4^+-$N \cdot ha^{-1}$ from the A1 horizon in plots treated with ammonium sulfate applied at the same rate (Figures 31 and 32; Appendix Table 37).

Nitrate (NO_3^-) Nitrogen

Although NO_3^- and NO_2^--N were determined together, the sum of the two are reported herein as NO_3^-. Levels of NO_3^- were low at all sampling times, and Table 14 indicates just how minor was the NO_3^- contribution to inorganic N levels.

Detectable levels of NO_3^- were not found to follow any particular treatment combination. It appeared that fertilization resulted in

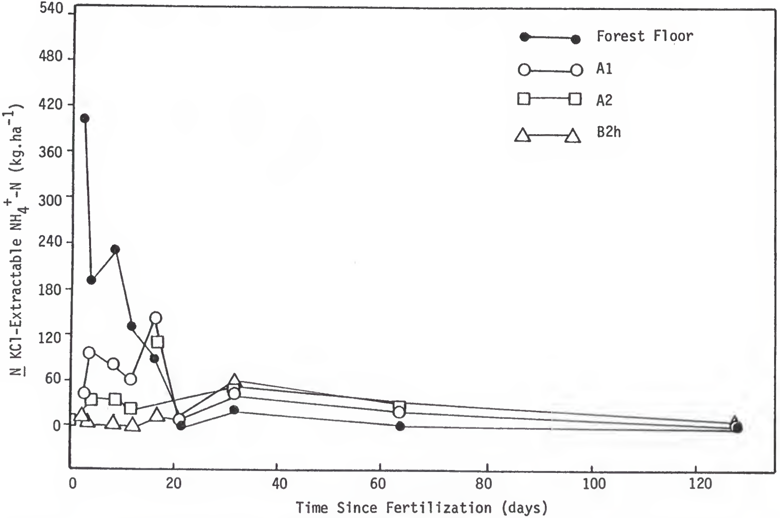

Figure 31. Distribution of N KCl-extractable NH_4^+ in the soil profile during 128 days following fertilization with ammonium sulfate at 400 kg N.ha^{-1}.

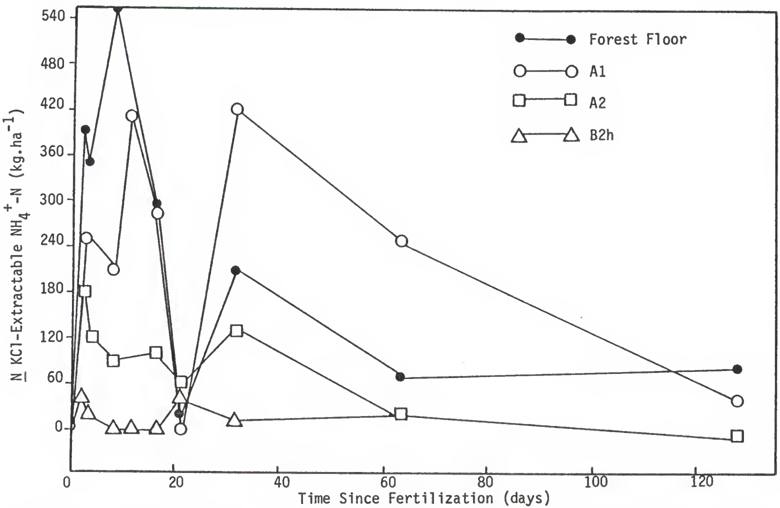

Figure 32. Distribution of N KCl-extractable NH_4^+ in the soil profile during 128 days following fertilization with urea at 400 kg N.ha^{-1}.

Table 14. Nitrate in water extracts of the forest floor, A1, and A2 horizons.

DST[1]	Fertilizer source				
	Nil	Ammonium sulfate		Urea	
	Rate of application (kg N.ha^{-1})				
	0	200	400	200	400
	kg NO_3^--N.ha^{-1}				
	Forest Floor				
0	0.0	0.1	0.3	0.2	0.3
2	0.1	0.7	2.1	0.2	0.1
4	0.0	0.6	0.9	0.2	0.0
8	0.1	0.3	1.2	0.0	0.0
16	0.0	0.1	0.2	0.1	0.1
64	0.0	0.0	0.0	0.0	0.1
128	0.0	0.0	0.0	0.0	0.2
	A1 Horizon				
0	0.2	0.6	0.4	1.5	0.5
2	1.6	3.7	2.4	1.3	0.9
4	0.3	1.3	2.1	1.1	0.2
8	1.0	0.0	0.0	0.9	0.5
16	0.7	2.5	0.3	1.6	1.0
64	0.0	0.1	0.0	0.2	0.5
128	0.1	0.0	0.0	0.0	0.9
	A2 Horizon				
0	2.5	0.0	3.5	0.0	1.0
2	5.9	2.4	2.1	2.2	1.0
4	0.3	1.3	2.1	1.1	0.2
8	1.0	0.0	0.0	0.9	0.5
16	0.7	2.5	0.3	1.6	1.0
64	0.1	0.2	0.3	0.2	0.6
128	0.0	0.0	0.2	0.0	0.1

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[1] Days since fertilization treatment.

elevated NO_3^- in both the forest floor and mineral horizons immediately after application and that ammonium sulfate treatments resulted in higher NO_3^- levels than the corresponding urea applications (Figures 33 and 34). The mineral horizons contained more NO_3^- than the forest floor. Initially the A2 horizon contained more NO_3^- than the A1 (Figure 35), but only until day 16 when significant rains leached this NO_3^- from the upper 50 cm of the soil profile. However, the concentration of NO_3^- in the A2 was always very much lower than in the A1.

Urea Nitrogen

Only urea applied at 400 kg $N \cdot ha^{-1}$ resulted in any appreciable quantity of water-extractable urea and this amounted to only approximately 10% of the applied urea 2 and 4 days after application. Distribution of urea was essentially confined to the forest floor (Figure 36) with some downward movement to the A1 and A2 horizons (Figure 37).

Water-Extractable Organic Nitrogen

When the soil was shaken with water during the extraction procedure considerable dispersion took place, and these extracts remained dispersed if left standing. When KCl was used as the extraction solution, the extracts flocculated upon standing following shaking, resulting in less dispersion of the soil colloids.

The sum of $NH_4^+ + NO_3^-$ was subtracted from the extract total N to provide a measure of the soluble organic N. Although the

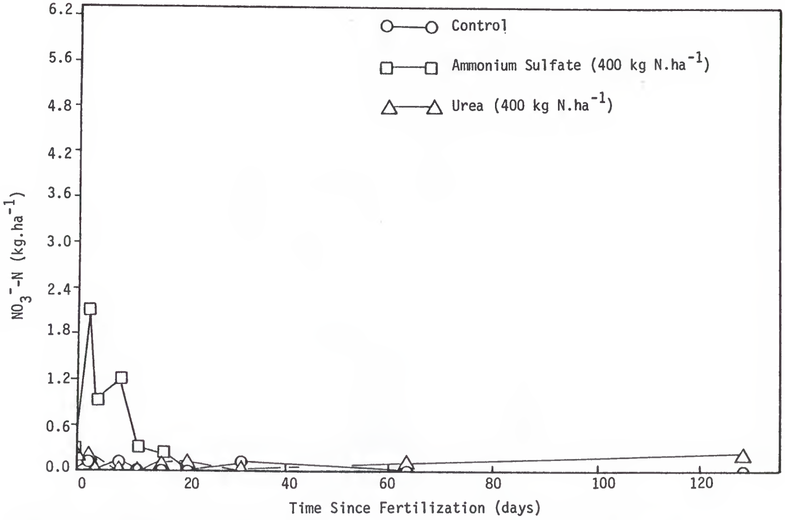

Figure 33. Nitrate in the forest floor during 128 days following fertilization.

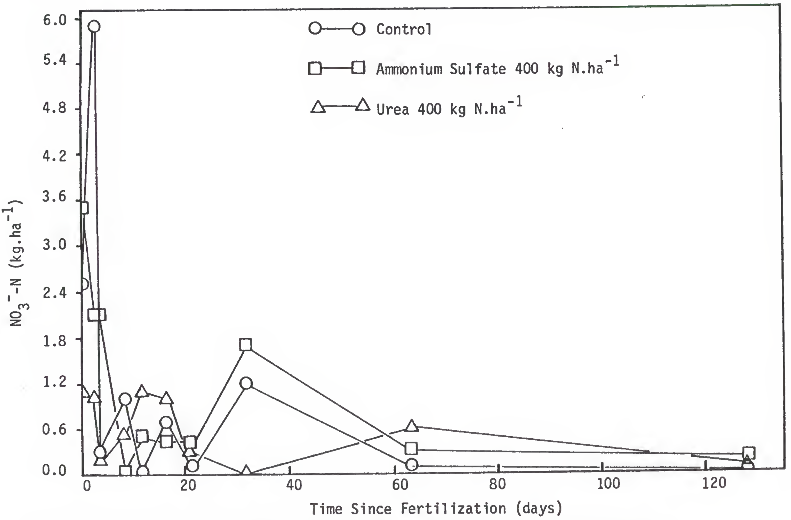

Figure 34. Nitrate in the A2 horizon during 128 days following fertilization.

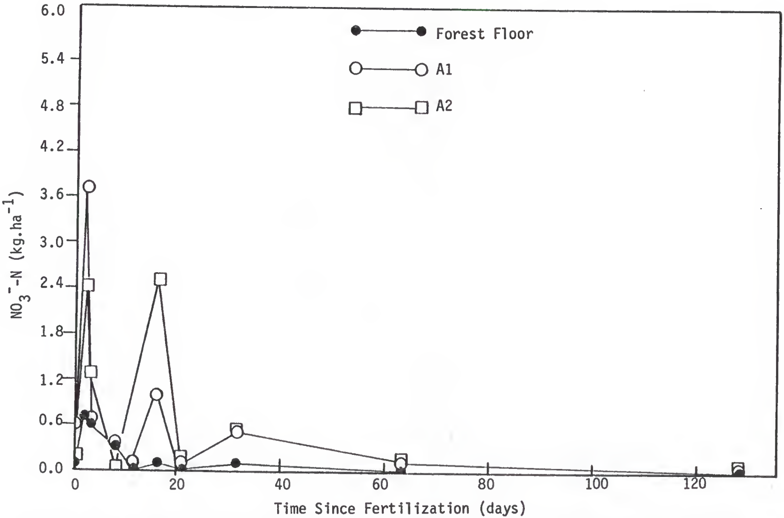

Figure 35. Nitrate in the surface horizons during 128 days following fertilization with ammonium sulfate at 200 kg N.ha^{-1}.

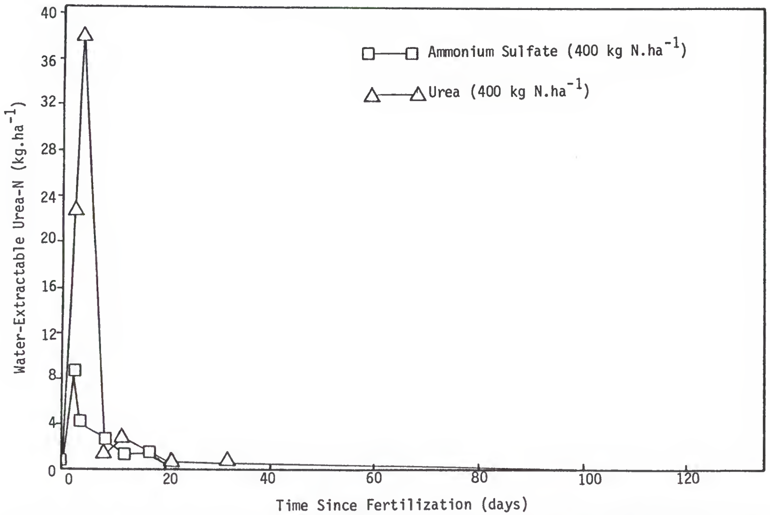

Figure 36 . Water-extractable urea in the forest floor during 128 days following fertilization.

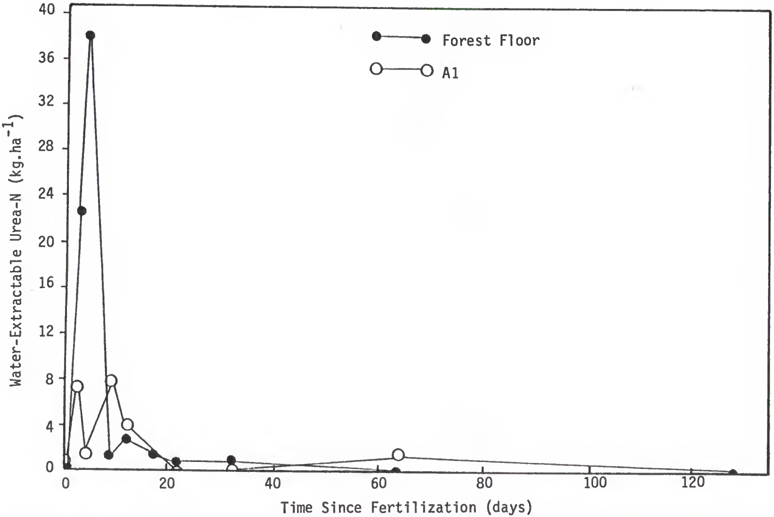

Figure 37. Distribution of water-extractable urea during 128 days following fertilization with urea at 400 kg N.ha^{-1}.

concentration of water-extractable organic N was clearly greatest in the forest floor extracts (Figure 38) the distribution of water-extractable organic N was uniform from horizon to horizon with some increase in the A1 and A2 horizons with time (Figure 39). Water-extractable organic N clearly decreased in the forest floor with time following fertilization (Figure 39).

Water-Extractable Cations

Water-extractable cations were determined on soil extracts and the results compared with double acid extractable values for the same soil horizon (Table 15). The greatest concentration of cations was found in the forest floor extracts, but total horizon contents were greater for the mineral horizons A1, A2, and B2h. Fertilizer applications resulted in the mobilization of Ca, Mg, K, and Na. Ammonium sulfate applications resulted in markedly increased cation concentrations initially (Figure 40). Mobilization of cations was most pronounced from the forest floor following applications of ammonium sulfate. Potassium, Ca, and Mg displayed a similar pattern of mobilization from the litter, and this pattern is represented by the change in Ca content in the forest floor depicted in Figure 41.

When urea was applied cations were not mobilized to the same extent as seen with ammonium sulfate applications (Figure 40). Calcium mobilization in the forest floor after urea additions was less than the observed increase in untreated plots, resulting from rains after day 16 (Figure 40). Calcium, Mg, and K were mobilized and transported down the profile as a result of urea fertilization, with

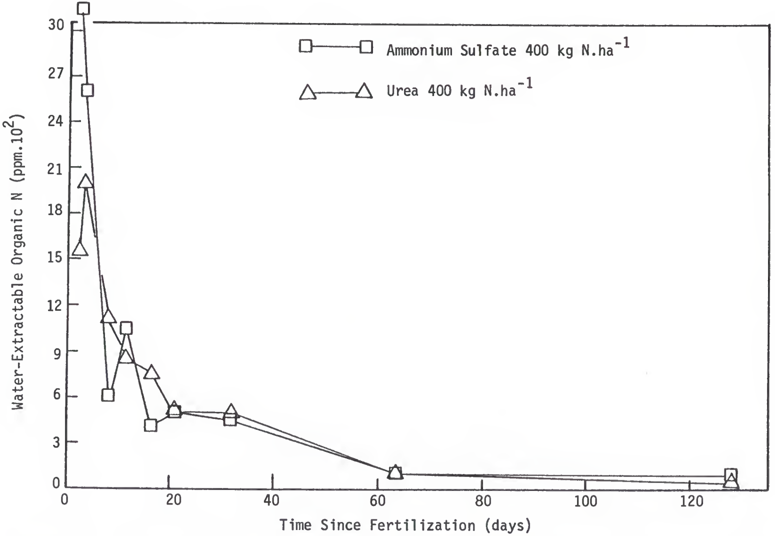

Figure 38 . Concentration of water-extractable organic N during 128 days following fertilization.

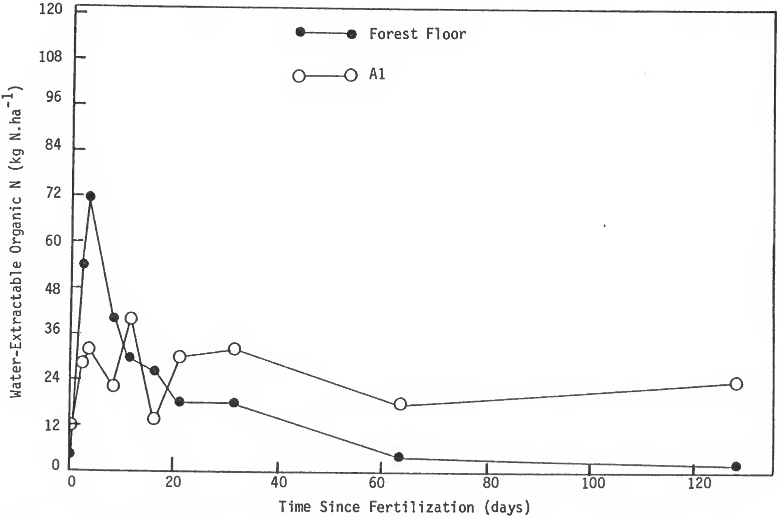

Figure 39. Water-extractable organic N during 28 days following application of 400 kg urea-N.ha^{-1}.

Table 15. Water and double-acid extractable cations and phosphorus from unfertilized control plots.

Soil horizon	Extractable cations and phosphorus						
	Al	Ca	Mg	K	Na	P	TCAT[2]
	Double-acid extractable cations ------------ppm (ODW)------------						
FF[3]	--	--	--	--	--	--	--
A1	51	100	21	10	13	2	195
A2	13	26	5	3	9	1	57
B2h	670	31	5	6	12	13	737
	Water-extractable cations ------------ppm (ODW)------------						
FF	24	150	77	219	150	--	620
A1	0	5	1	7	10	--	23
A2	0	2	0	4	5	00	11
B2h	6	8	3	6	10	--	33
	Water-extractable cations ------------$kg.ha^{-1}$------------						
FF	1	5	3	8	5	3	22
A1	0	7	2	10	15	6	34
A2	0	7	0	13	16	4	36
B2h	6	9	3	6	12	1	36

[1] Double-acid extractable (Mehlich, 1953).

[2] Sum of Al, Ca, K, Mg, plus Na.

[3] Forest floor.

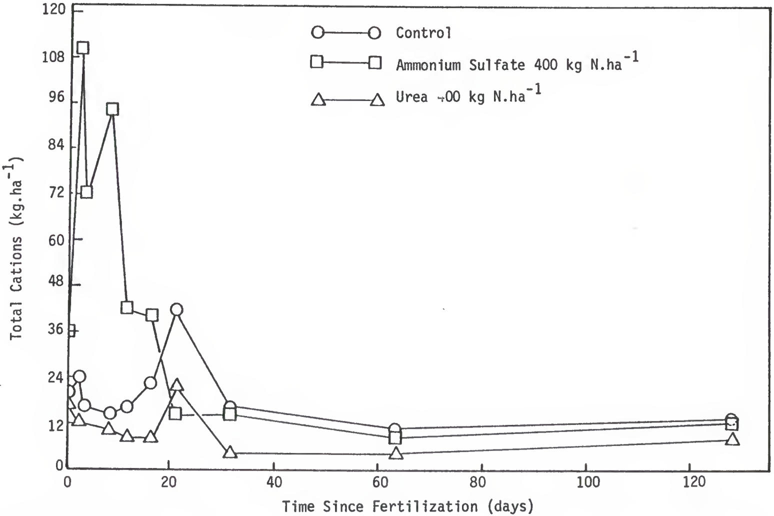

Figure 40. Total water-extractable cations from the forest floor during 128 days following fertilization.

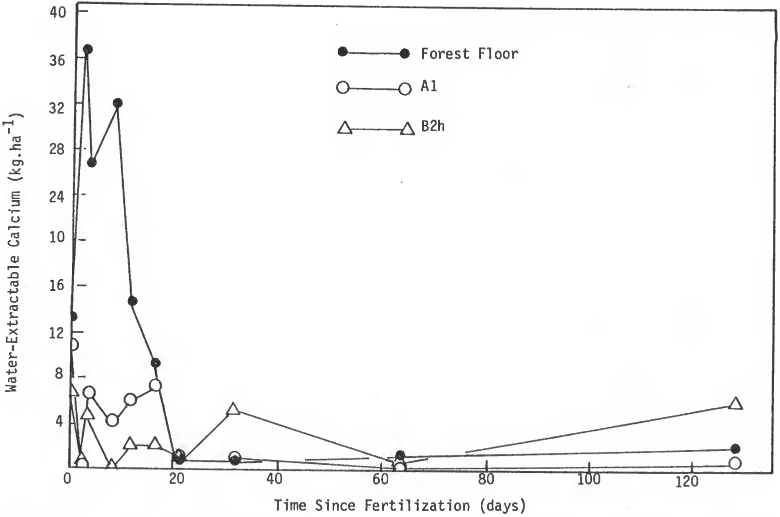

Figure 41. Distribution of water-extractable calcium during 128 days following fertilization with ammonium sulfate at 400 kg N.ha^{-1}.

significant increases in the Al detected 21 days after fertilizer application, and in the A2 and B2h 64 days after treatment. By day 128, levels in all horizons were similar to pretreatment values. The pattern of movement of K is shown following urea application of 400 kg N$\cdot$ha^{-1} (Figure 42). Sodium contents were found to be highest in the A2 rather than A1, 21 days after fertilization, with either ammonium sulfate or urea (Figure 43). Aluminum content was greatest in the B2h regardless of fertilizer treatment. Some Al appeared to be mobilized from the forest floor following urea fertilization, resulting in greater accumulations in the B2h (Figure 44).

The distribution of the sum total of these previously mentioned cations showed accumulation in the mineral horizons up until day 21 and a return to pretreatment levels by day 128 (Figure 45). This pattern was common to all treatment combinations, showing absolute increases initially, for high levels of N application.

Phosphorus was mobilized from the forest floor and mineral horizons equally by ammonium sulfate or urea, resulting in a peak content in the A1 horizon 16 days after treatment, followed by a more diffuse peak in the A2 horizon 32 days after fertilization (Figure 46).

Horizon contents of all cations and P rapidly increased following fertilization and then declined exponentially with time (or cumulative rainfall). This decline appeared to be seasonal and could be in response to increased leaching, increased plant uptake, or adsorption onto exchange sites, where they would not be easily extracted with water.

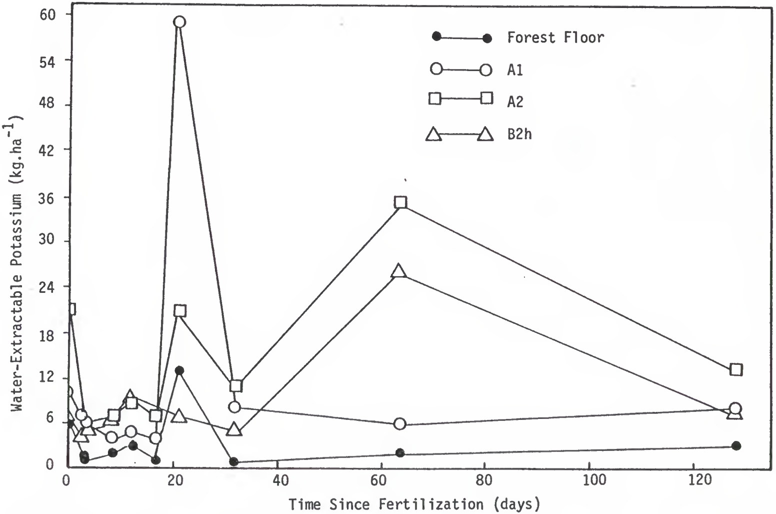

Figure 42. Distribution of water-extractable potassium during 128 days following fertilization with urea at 400 kg N.ha^{-1}.

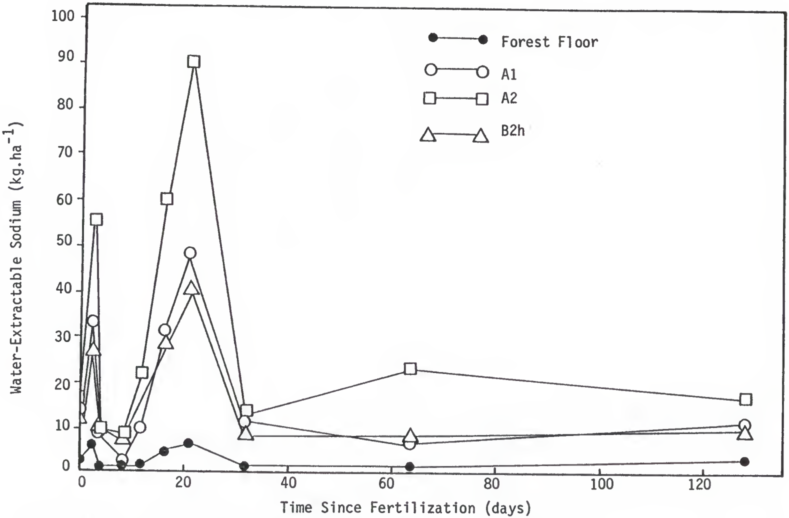

Figure 43. Distribution of water-extractable sodium during 128 days following fertilization with urea at 400 kg N.ha^{-1}.

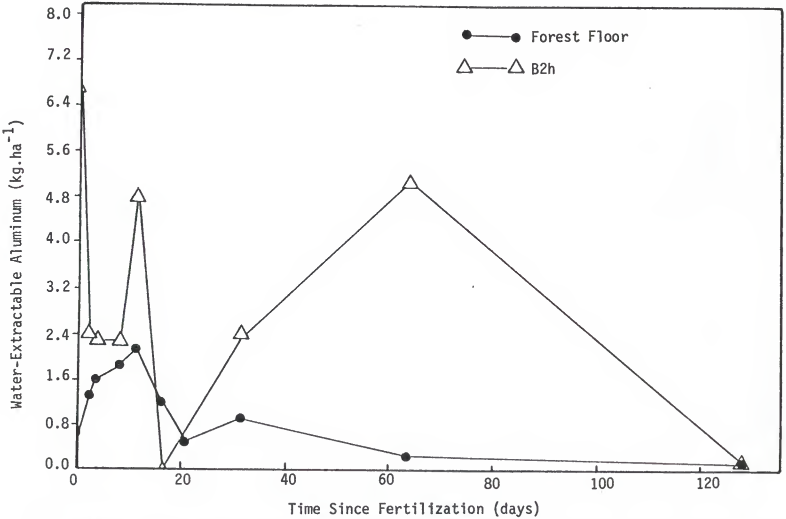

Figure 44. Distribution of water-extractable aluminum during 128 days following fertilization with urea at 400 kg N.ha^{-1}.

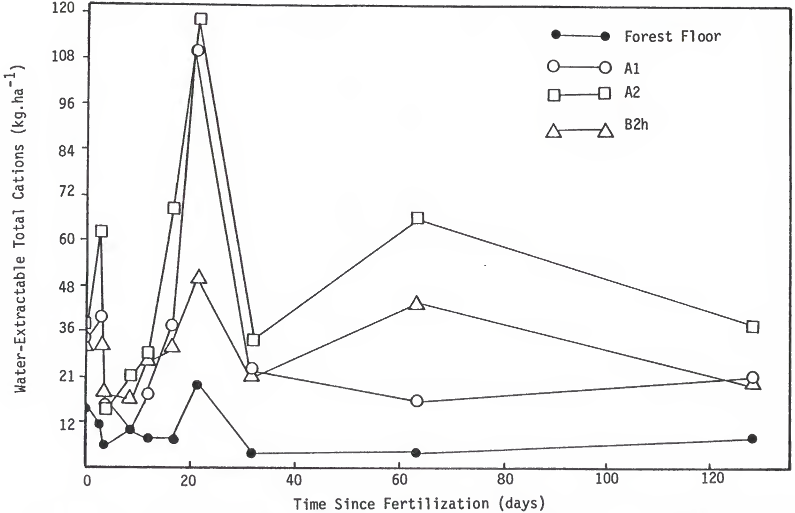

Figure 45. Distribution of water-extractable total cations during 128 days following fertilization with urea at 400 kg N.ha^{-1}.

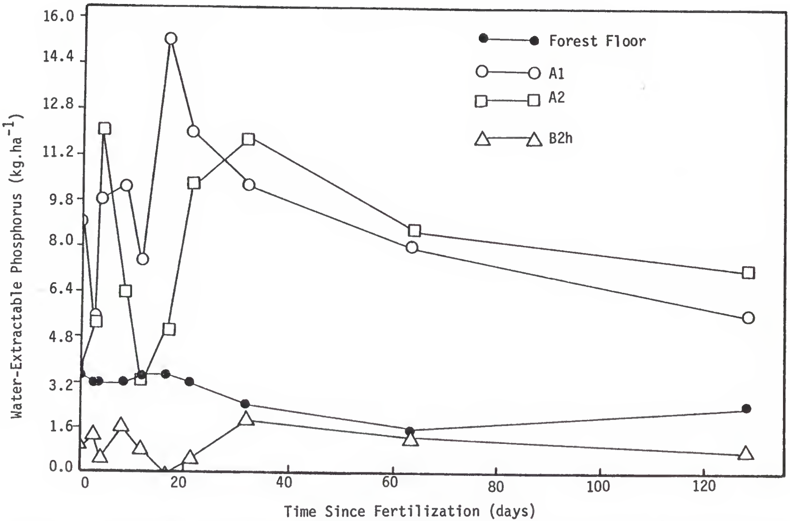

Figure 46. Distribution of water-extractable phosphorus during 128 days following fertilization with ammonium sulfate at 200 kg N.ha^{-1}.

Water-Extractable Total Carbon

Ammonium sulfate additions resulted in a mobilization of cations from the forest floor, but urea additions usually did not (Figure 40). However, urea additions did result in more water-extractable C from the forest floor samples (Figure 47). This was a principal difference between the two N sources. Extractable total C from the mineral horizons did not appear to be as strongly affected by fertilizer source as it was in the forest floor. In control plots each of the mineral horizons appeared to contain more extractable total C than the forest floor (Figure 48), and urea applied at 400 kg $N.ha^{-1}$ was the only treatment to change this basic relationship. The high level of urea application resulted in rapid mobilization of C from the forest floor and a subsequent accumulation in the A1 and B2h by day 21, as a result of heavy rain. By day 32 levels had returned to pretreatment values (Figure 49).

Carbon:Nitrogen (C:N) Ratio

Carbon:nitrogen ratios (C:N) were calculated for soil samples collected prior to fertilization and these ratios were compared with extract C:N ratios (Table 16). A strong relationship was established between soil and extract C:N ratios (Figure 50). The relationship between extract total C and N KCl-extractable mineral N was also tested and the relationship was not as well defined.

The extract C:N ratios following fertilization were markedly reduced in all horizons (Tables 17 and 18). Extract C:N ratio reductions in the forest floor were greatest and persisted through 64

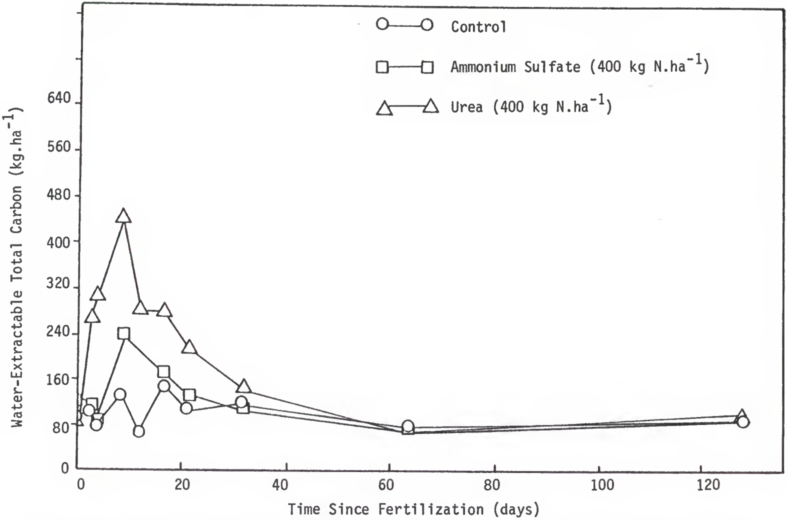

Figure 47. Water-extractable total carbon in the forest floor during 128 days following fertilization.

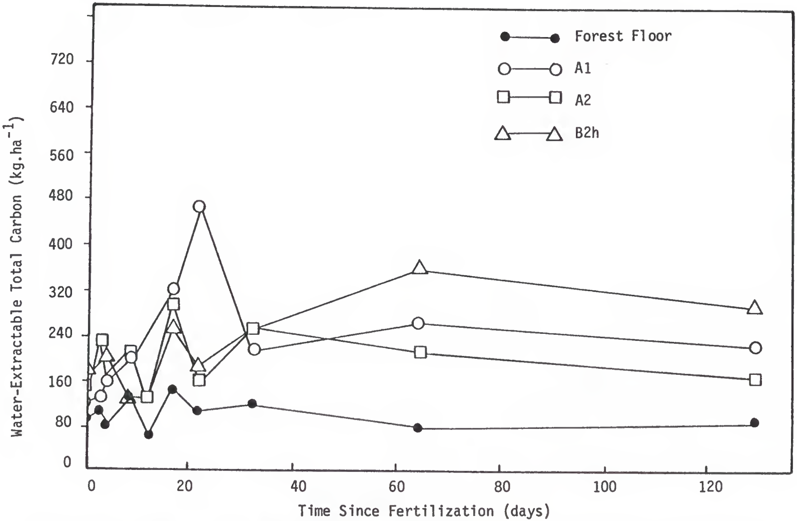

Figure 48. Distribution of water-extractable total carbon in the profile of control plots during 128 days following fertilization.

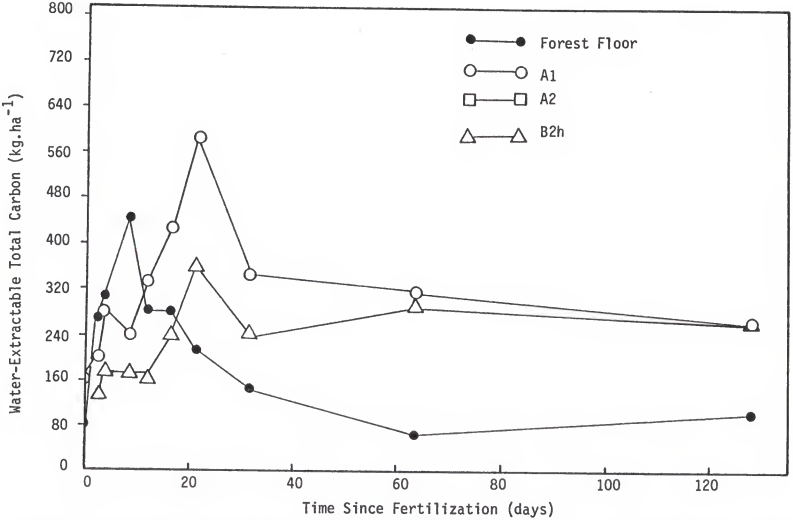

Figure 49. Distribution of water-extractable total carbon in the soil profile during 128 days following fertilization with urea at 400 kg N.ha^{-1}.

Table 16. Carbon:nitrogen (C:N) ratios from soil and water extracts for mineral horizons.

	OC[1] %	TN[2] %	C:N[3]	EX C:N[4]
FF	--	--	--	14
A1	1.24	.04	31:1	12:1
A2	0.22	.009	24:1	10:1
B2h	2.08	.05	42:1	15:1

[1] Soil total organic carbon.

[2] Soil Kjeldahl nitrogen.

[3] C:N = OC ÷ TN.

[4] EX C:N = Extract total OC ÷ extract total nitrogen.

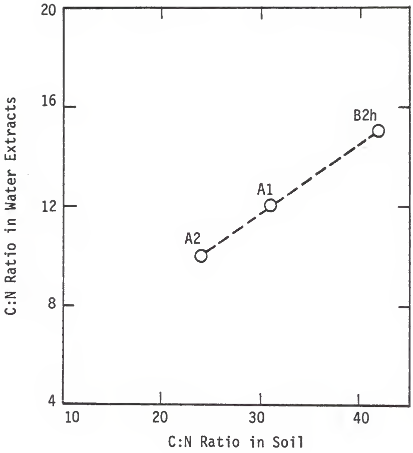

Figure 50. Relationship between The C:N ratio of soil and soil water extracts for three mineral horizons in Wauchula fine sand.

Table 17. Ratio of total water extractable carbon to nitrogen (C:N) in the forest floor (FF) and A1 horizon.

Horizon	DST[1]	Fertilizer source								
		Nil					Urea			
		Rate of application (kg N.ha^{-1})								
		0	100	200	300	400	100	200	300	400
FF	0	14	13	17	18	13	13	12	12	14
	2	14	1.2	0.7	0.4	0.4	3.4	3.7	3.2	3.2
	4	14	1.4	1.0	0.6	0.4	4.2	4.3	3.2	3.4
	8	29	1.8	2.7	0.7	1.3	10	7	5	5
	12	8	1.7	0.8	0.6	0.7	5	5	5	5
	16	25	6	3	2.6	2.5	8	10	8	7
	21	21	9	8	5	6	9	7	10	11
	32	20	14	5	5	4	5	7	6	5
	64	25	18	16	12	13	15	10	7	8
	128	44	43	20	28	29	28	24	21	14
A1	0	10	11	11	12	11	17	12	14	11
	2	6	4	3	3	4	5	4	7	4
	4	16	4	5	5	2	7	27	5	6
	8	19	11	5	3	4	12	8	10	6
	12	11	6	2	3	2	7	5	6	5
	16	28	11	9	7	3.3	4	19	9	12
	21	46	21	31	9	12	26	19	7	18
	32	24	17	9	7	5	12	14	11	6
	64	18	45	18	24	17	30	18	11	11
	128	31	120	14	45	13	25	22	15	9

---

[1] Days since fertilization.

Table 18. Ratio of total water-extractable carbon to nitrogen (C:N) in A2 and B2h horizons.

Horizon	DST[1]	Fertilizer source								
		Nil	Ammonium sulfate				Urea			
		Rate of application (kg N.ha^{-1})								
		0	100	200	300	400	100	200	300	400
A2	0	11	--	12	9	8	11	9	9	12
	2	11	5	3	4	2	6	5	7	2
	4	19	9	8	4	4	5	13	7	7
	8	36	7	7	4	6	10	9	9	7
	12	8	4	3	2	3	17	5	4	11
	16	17	17	5	8	4	8	17	13	16
	21	13	189	109	11	57	12	20	23	32
	32	13	6	6	8	6	16	11	13	6
	64	6	21	11	6	7	3	6	6	8
	128	13	13	10	17	3	18	16	6	22
B2h	0	18	16	15	16	17	14	16	12	14
	2	10	6	7	12	6	8	9	8	6
	4	28	7	12	11	11	17	14	33	11
	8	18	22	34	17	27	23	16	20	14
	12	15	12	9	9	9	15	14	9	10
	16	25	29	25	16	28	42	11	24	24
	21	29	58	28	23	20	43	55	99	19
	32	21	19	8	10	3	21	23	17	35
	64	31	38	24	19	9	24	16	29	18
	128	74	21	54	14	12	28	14	22	30

---

[1] Days since fertilization.

days. The reductions in mineral horizons were not as great in magnitude nor did they persist as long as in the forest floor. The reductions in extract C:N in the B2h horizon were associated with ammonium sulfate fertilization and only occurred following rain on day 12 and day 32 (Table 18).

Predictive Models

Linear models were used in an attempt to predict the observed decay in most of the soil nitrogen variables determined. The general form of all linear models was

$$Y = \beta_o + \beta_1 R + \beta_2 R^2 + \beta_3 DR + \beta_4 DR^2 + E$$

where D = fertilizer source (NFERT)

NFERT = 1 or 2 for ammonium sulfate and urea, respectively

R = rate of application for each source

D = NFERT - 1; therefore,

D = 1 when NFERT = 2, and

D = 0 when NFERT = 1 and consequently the regression for NFERT = 1 will have the form

$$Y = \beta_o + \beta_1 R + \beta_2 R^2 + E$$

and if NFERT = 2 the regression is

$$Y = \beta_o + (\beta_1 + \beta_3)R + (\beta_2 + \beta_4)R^2 + E$$

The second tier of a two tiered model consisted of linear and quadratic terms for days since treatment application (DST). A list of dependent variables used in the general predictive models, incorporating time in a second tier of interaction terms, is shown in Appendix Tables 38, 39 . Models of the same general form were used having inverted the time term DST, or by taking the log transformation of the dependent variable to be analyzed. All horizons were analyzed separately, using a least squares means option (Barr et al., 1976). Since most parameters tested showed an exponential decay with time, log transformations of the parameters were well explained by the general model. Quadratic terms for fertilizer rate were dropped from the general model as they did not contribute significantly to overall fit. The general form then became

$$\begin{aligned}\text{Log } Y = {} & \beta_0 + \beta_1 B + \beta_2 R + \beta_3 D x R + \beta_4 T \\ & + \beta_5 DST + \beta_6 DST x DST + \beta_7 R x DST \\ & + \beta_8 R x D x DST\end{aligned}$$

where B = blocks
D = fertilizer source
R = fertilizer rate
T = lack of fit term
DST = days since treatment

The linear model utilizing log transformations of the soil N data fitted best for the forest floor; in addition, most dependent soil N and C variables for the mineral horizons were well modelled by the linear combination of variables (Table 19). Other soil chemical data were also analyzed, using the same model for each soil profile horizon.

Table 19. Regression F probability level for the linear models used to analyze soil chemical data.

HOR	Y	R^2	C.V.[2]	Sig.[3]	HOR	R^2	C.V.	Sig.
FF	LSTN[1]	0.38	3	***	A1	0.52	5	***
	LEXTN	0.86	8	***		0.48	21	***
	LEXNH4N	0.74	21	***		0.48	61	***
	LEXNH4K	0.74	20	***		0.66	40	***
	LEXNO3N	0.67	119	***		0.68	69	***
	LEXURN	0.49	59	***		0.34	327	*
	LONWE	0.77	9	***		0.17	33	*
A2	LSTN	0.22	7	***	B2h	0.28	4	***
	LEXTN	0.23	37	***		0.17	28	*
	LEXNH4N	0.38	130	***		0.23	135	**
	LEXNH4K	0.65	46	***		0.43	67	***
	LEXNO3N	0.45	65	***		0.67	53	***
	LEXURN	0.56	83	***		0.42	106	***
	LONWE	0.13	61	NS		0.13	32	NS

---

[1] See Appendix Table to explain dependent variables.

[2] Coefficient of variation.

[3] Significance of model. *** = 99.9% level of probability.
** = 99% level of probability.
* = 95% level of probability.

The predictive model provided very highly significant results for water-extractable P, water-extractable cations except Al, and for extract C:N ratios (Table 20).

Table 20. Regression F probability level for the linear models used to analyze soil chemical data, other than nitrogen, on forest floor samples.

y^1	R^2	C.V.^{2}	Sig.^{3}
LEXPH	0.83	5	***
LCAHA	0.77	104	***
LMgHA	0.79	198	***
LKHA	0.67	37	***
LNaHA	0.44	46	***
LAlHA	0.29	464	*
LTCATHA	0.69	20	***
LPHA	0.27	47	***
LEXTCHA	0.48	9	***
LEXC:N	0.82	32	***

[1] List of dependent variables in Appendix Table 38.

[2] Coefficient of variable.

[3] Significance of model.
*** = 99.9% probability level
** = 99% probability level
* = 95% probability level.

Nitrous Oxide Evolution

Field Experiment #2

Gas samples were analyzed for N_2O on a regular basis, from both field experiment #2 and #3.

Background levels of N_2O evolution were measured from control plots over time, and levels of N_2O evolved as a result of fertilization, were also determined. Nitrous oxide evolution from field experiment #2 was measured from plots treated with ammonium sulfate and urea at 200 and 400 kg $N.ha^{-1}$.

Levels of N_2O measured from field experiment #2 showed a sharp rise from plots treated with ammonium sulfate at 400 kg $N.ha^{-1}$, 29 days after fertilization (Figure 51). This was a single recording in time from replicated sampling traps. At 56 days after fertilization the maximum recording of N_2O evolution was made from plots treated with urea at 400 kg $N.ha^{-1}$. This peak of N_2O coincided with a heavy rainstorm two days previously when 54 mm of rain fell (Appendix Table 40; Figure 16). Nitrous oxide evolution returned to lower levels in the following 20 day period and did not peak again in response to succeeding thunderstorms (Figure 52; Table 21).

Soil cores taken from the plots treated with urea at 400 kg $N.ha^{-1}$, at the time of peak N_2O production (which occurred 57 days after fertilization), revealed the presence of NO_3^- in the soil. The concentrations and total amounts of NO_3^- do not appear to be very great, but just the fact that nitrification had taken place is of significance. Details of sampling at day 57 are recorded in Table 22.

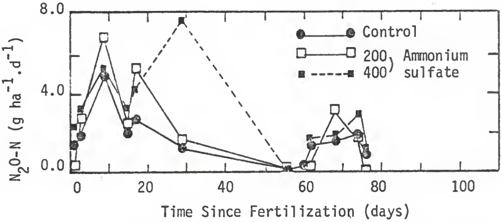

Figure 51. N_2O evolution following ammonium sulfate fertilization in field experiment #2.

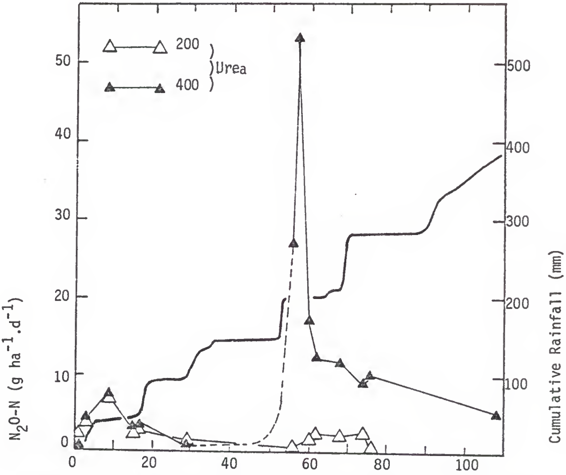

Figure 52. N_2O evolution and cumulative rainfall following urea fertilization in field experiment #2.

Table 21. Nitrous oxide evolution following urea or ammonium sulfate fertilization (field experiment #2).

DST[1]	Fertilizer source Nil	Ammonium sulfate Rate of application (kg $N.ha^{-1}$)		Urea	
	0	200	400	200	400
	$g\ N_2O-N.ha^{-1}.day^{-1}$				
1	1.2	0.0	2.2	1.9	0.6
3	1.7	2.6	3.0	3.6	4.1
9	4.7	6.8	5.0	6.9	7.1
15	1.8	2.4	3.1	2.1	2.5
17	2.6	5.2	4.1	2.5	2.9
29	1.1	1.5	7.6	1.5	1.2
56	0.0	0.0	0.0	0.0	26.6
57	--	--	--	--	52.8
60	0.2	0.6	0.0	1.5	16.8
62	1.2	0.6	1.3	2.1	12.1
68	1.4	2.9	1.5	1.9	11.3
74	1.8	1.6	2.8	2.3	8.9
76	0.7	0.0	0.7	0.4	9.9
108	--	--	--	--	4.8

[1] Days since fertilization.

Table 22. Nitrate and pH in soil profile samples 57 days after fertilization of experiment #2 with 400 kg urea-$N.ha^{-1}$.

Soil horizon	Soil pH	NO_3^- (ppm)	NO_3^- (kg $N.ha^{-1}$)
FF[1]	5.46	2.39	0.08
A1	5.29	2.35	3.23
A2	5.39	2.47	9.70
B2h	4.61	1.43	1.63

[1] Forest floor.

The results from field experiment #2 were analyzed in order to partition the variation in field observations and to determine whether the treatment effects differed between sampling times. Sources of variation were due to replications, treatment combinations, and time since fertilization (Table 23).

Table 23. Sources of variation in field observations of N_2O evolution in field experiment #2.

Source	df	MS	F
Replicates	5	235	20***[1]
Treatment	4	297	67***
Time	13	70	6***
Treatment x Time	48	127	11***
Error	398	117	

[1] ***Significant at the 99.9% level.

Since the interaction term treatment x time was highly significant, all sampling dates were analyzed separately, and the means for fertilizer rate and fertilizer source separated by a multiple range procedure. Urea applications resulted in significantly more denitrification from day 56 through to day 76. The rate of application of 400 kg $N.ha^{-1}$ urea resulted in the significant mean N_2O evolutions for the period day 56-76 (Tables 24 and 25). Urea applied at 200 kg $N.ha^{-1}$, and both rates of ammonium sulfate application were no different from the control values for N_2O evolution. On day 29 after fertilization ammonium sulfate applied at 400 kg $N.ha^{-1}$ resulted in a significantly

Table 24 . Average evolution of N_2O from urea and ammonium sulfate plots during 108 days following fertilization.

Time since treatment (days)	Fertilizer[1]		Rate (kg $N.ha^{-1}$)[2]		
	Ammonium sulfate	Urea	0	200	400
	------------------g N_2O-$N.ha^{-1}.day^{-1}$				
3	2.5^a	3.3^a	1.9^b	3.2^{ab}	3.6^a
9	6.0^a	4.8^a	4.7^a	6.1^a	5.4^a
15	2.3^a	2.4^a	1.9^a	2.5^a	2.8^a
17	3.9^a	2.8^a	2.7^a	3.3^a	4.0^a
29	2.1^a	1.0^a	0.7^b	1.0^b	3.0^a
56	0.3^b	6.0^a	0.0^b	0.2^b	9.1^a
57	--	11.9	--	--	17.8
60	0.3^b	4.0^a	0.2^b	0.8^b	5.5^a
62	0.6^b	3.5^a	0.7^b	0.9^b	4.5^a
68	1.2^b	3.3^a	0.9^b	1.6^b	4.3^a
74	1.5^a	2.9^a	1.2^b	1.5^b	3.9^a
76	0.5^b	2.5^a	0.4^b	0.4^b	3.6^a
108	--	3.2	--	--	4.9

[1] Average of all rates.

[2] Average of both sources.

Table 25. Average evolution of N_2O from five treatment combinations of urea and ammonium sulfate applied at 200 and 400 kg $N.ha^{-1}$ during 108 days following fertilization.

Time since treatment (days)	Nil	Ammonium Sulfate		Urea	
	kg $N.ha^{-1}$				
	0	200	400	200	400
	g $N_2O\text{-}N.ha^{-1}.day^{-1}$				
3	1.9^{b}	2.6^{ab}	3.1^{ab}	3.7^{ab}	4.2^{a}
9	4.7^{a}	7.1^{a}	5.2^{a}	5.1^{a}	5.7^{a}
15	1.9^{a}	2.7^{a}	3.2^{a}	2.3^{a}	2.5^{a}
17	2.7^{a}	5.3^{a}	3.7^{a}	2.6^{a}	3.0^{a}
29	0.7^{b}	0.9^{b}	5.2^{a}	1.0^{b}	0.8^{b}
56	0.0^{b}	0.3^{b}	0.4^{b}	0.2^{b}	17.7^{a}
57	--	--	--	--	35.6
60	0.2^{b}	0.7^{b}	0.0^{b}	1.0^{b}	11.1^{a}
62	0.7^{b}	0.4^{b}	0.9^{b}	2.5^{b}	8.1^{a}
68	0.9^{b}	2.0^{b}	0.9^{b}	1.2^{b}	7.6^{a}
74	1.2^{b}	1.2^{b}	2.0^{b}	1.8^{b}	5.9^{a}
76	0.4^{b}	0.5^{b}	0.5^{b}	0.3^{b}	6.6^{a}
108	--	--	--	--	9.7

greater amount of N_2O evolution than all other treatments (Table 25).

Field Experiment #3

This field experiment was designed to assess three N sources for potential losses by denitrification. Ammonium sulfate, ammonium nitrate, and urea were the three sources. Nitrate N was applied in this field experiment at the rate of 100 kg $N.ha^{-1}$. The experiment was initiated 23 days after field experiment #2 and ran concurrently with #2.

There was no N_2O evolution initially because the soil was dry (point) (A) on Figure 53). The maximum evolution occurred in response to heavy rain 31 days after fertilization (point (B) on Figure 53). Nitrous oxide evolution continued to lag behind significant storms (point (C)), and then decrease in dry weather (point (D)). Peak N_2O evolution was 11 g $N_2O\text{-}N.ha^{-1}.day^{-1}$ from 100 kg $NO_3^-\text{-}N$ applied in ammonium nitrate (Table 26). This rate of 11 g was compared with the peak rate of 53 g $N_2O\text{-}N.ha^{-1}.day^{-1}$ following application of 400 $kg.ha^{-1}$ urea-N. All peak N_2O evolution was shortlived.

Nitrous oxide evolution in field experiment #3 was also subjected to analysis of variance. Fertilizer source and time since treatment both contributed significantly to N_2O evolution (Table 27). Nitrous oxide concentrations were determined for each sampling date.

Results of Duncan's Multiple Range tests indicate that ammonium nitrate gave significantly greater N_2O evolution for a major part of the 85 day sampling period (Table 26).

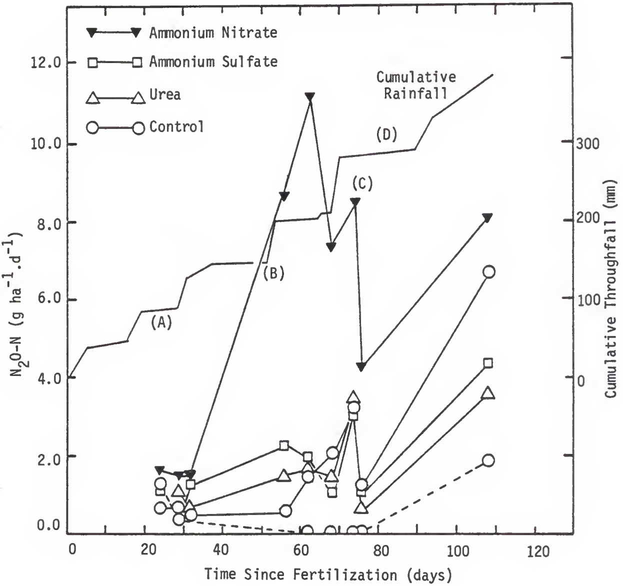

Figure 53. Nitrous oxide evolution in relation to time and throughfall following fertilization with ammonium nitrate, urea, and ammonium sulfate at 200 kg N.ha-1.

Table 26. Nitrous oxide evolution from field experiment #3 following fertilization with three N sources at the rate of 200 kg N.ha^{-1}.

Time since treatment (days)	Fertilizer source (200 kg N.ha^{-1})			
	Nil	Ammonium sulfate	Urea	Ammonium nitrate
	------------------g N_2O-N · ha^{-1}.day--------------------			
1	0.6^{a}[1]	1.0^{a}	0.6^{a}	1.5^{a}
6	0.6^{a}	0.4^{a}	1.0^{a}	1.4^{a}
9	0.4^{a}	1.2^{a}	0.6^{a}	1.4^{a}
33	0.5^{b}	2.2^{ab}	1.4^{b}	8.5^{a}
39	1.4^{b}	2.0^{b}	1.6^{b}	11.1^{a}
45	2.0^{b}	1.5^{b}	1.4^{b}	7.2^{a}
51	3.2^{a}	2.5^{a}	3.4^{a}	8.4^{a}
53	1.2^{a}	1.0^{a}	0.6^{a}	4.2^{a}
85	2.3^{a}	4.3^{a}	3.5^{a}	8.0^{a}

[1] Means with the same letter are not significantly different at the 95% probability level using Duncan's Multiple Range test.

Table 27. Analysis of N_2O evolution from field experiment #3, for all observations.

Source	df	MS	F
Replicate	1	1.3	0.3 NS[1]
Fertilizer	3	78.7	18.1***
Fertilizer x replicate	3	5.4	1.2 NS
Time	8	19	4.4*
Fertilizer x time	24	5.1	0.3 NS
Error	32	4.3	
Total	71		

[1] NS = Not significant.
***Significant at 99.9% level of probability.
*Significant at 95% level of probability.

DISCUSSION

The effects of urea and ammonium sulfate applications to a flatwoods pine plantation will be discussed in terms of the impacts of fertilization on the extent of N transformations, cation mobilization, and gaseous N losses as they are affected by changes in soil acidity and soluble carbon. The sources of gaseous N losses include NH_3 volatilization and denitrification.

Nitrogen Transformations

Ureolysis and Ammonification

Urea fertilizer solution was sprayed onto the forest floor to ensure a more uniform N application than the broadcasting of prilled solid urea. The spray application resulted in a rapid hydrolysis reaction, which was demonstrated by higher initial NH_3 volatilization from sprayed subplots, than the prill treated plots (Figure 13). The temporary delay in ureolysis of prilled urea indicated that water was limiting for the reaction in this instance. Derome (1979) suggested that the application of urea to a dry forest floor would result in a below normal level of NH_3 volatilization, indicating inhibition of ureolysis. However, prilled urea persisted unhydrolyzed longer than urea which was sprayed, resulting in smaller cumulative losses, particularly when applied at the lower levels (Figure 14).

The site for maximum urease activity was found by Derome (1975) to be at the soil-litter interface, and the results of this current investigation revealed little or no penetration of unhydrolyzed urea through the forest floor, confirming the earlier work of Derome (1975). Limited availability of urease, as suggested by Volk (1970) may explain why the loss of NH_3 from the 300 kg $N.ha^{-1}$ application was as great as from heavier applications. Although initially a lack of moisture may have limited ureolysis from prilled applications of urea the quantity of water-extractable urea fell very rapidly following the first rainstorm 12 days after fertilization, also indicating that the availability of urease was not seriously lacking (Figures 36 and 37).

Ammonification results from the hydrolysis of urea fertilizer, and ammonium sulfate undergoes dissociation in water, both processes providing an instantaneous supply of NH_4^+ to the forest soil.

Other major differences between the two fertilizers spring from the decreased acidity associated with ammonium carbonate formation following ureolysis, compared with an increase in acidity following applications of ammonium sulfate. Important consequences of decreased acidity following urea applications include increased cation exchange capacity, as demonstrated by Huang (1978), who measured large increases in the CEC of forest floor materials when the pH was maintained at elevated values. Decrease in acidity in response to urea fertilization often results in increased levels of NH_3 volatilization and this effect will be discussed in a later section. Ammonium sulfate additions increased soil acidity which would have the opposite effect of urea on pH-dependent cation exchange capacity. If one assumes that soil acidity was all that inhibited N transformations, then the increased pH as a result of urea additions should have corrected this limitation. Conditions, therefore, should have been more conducive for nitrification in the event that NH_4^+ became available.

Urea and ammonium sulfate applications to the forest represent sources of NH_4^+ which may in turn become assimilated by the soil microflora, taken up by higher plants, leached, or become substrate for nitrification. The soil organic N which makes up a very large proportion of native N content of the soil may also be ammonified to provide NH_4^+ to be distributed between the various sinks mentioned above. Nitrogen fertilization can often lead to stimulation of ammonification of the native soil N reserves, resulting in a net increase in NH_4^+ available in the soil. Knowles (1975) mentioned an example where the application of up to 400 ppm of NH_4^+ resulted in the release of 1500 ppm KCl-extractable organic N. This effect, the release of a greater amount of N than initially applied,has been called the "priming effect." Priming of the soil organic N will therefore provide additional NH_4^+ to that which would be normally available for assimilation, transformation, and plant metabolism.

Analysis of soil total N is a relatively crude indication of changes brought about in the profile distribution of N as a result of fertilization, because such a measure of soil N change is buffered by a relatively large native soil total N value. However, measures of soil total N show a clear response to the rates of N application used in this study. Total N values in the forest floor increased most dramatically and the total N contents of the A1 horizon were increased by applications as low as 200 kg N.ha^{-1} of ammonium sulfate. The fertilizer additions, whether ammonium sulfate or urea, changed the relative distribution of total N in the A1 and B2h horizons, and the redistribution persisted during 128 days of the experiment (Figure 23 compared with 24).

The effects of fertilizer N additions and the ammonification of native organic N were more sensitively measured by analysis of water-extractable total N, water-extractable NH_4^+-N, and N KCl-extractable NH_4^+, than by soil total N. Water-extractable total N was strongly influenced by fertilizer source. Ammonium sulfate additions resulted in large increases in this form of N with lesser increases resulting from urea applications. However, the large increases were transient--lasting for no more than 21 days. The forest floor extracts contained a large proportion of the increase in water-extractable total N (Figures 26 and 27), and water-extractable NH_4^+ was the major form of N contributing to the water-extractable total N values (Figure 29). The small amounts of water-extractable NH_4^+ following urea additions apparently reflect the inability of water to remove NH_4^+ from the expanded cation exchange capacity. The NH_4^+ resulting from urea fertilization persisted in the soil, or in turn promoted ammonification of soil organic N for the duration of the experiment. This persistance of NH_4^+ with urea fertilization again demonstrated an effect of increased cation exchange capacity.

The persistance of NH_4^+ was greatest in the forest floor and A1 horizons as seen from the values of N KCl-extractable NH_4^+. The relative mobility of NH_4^+ following ammonium sulfate applications was demonstrated by Overrein (1971) who recovered 96% of a 250 kg N.ha^{-1}

application of NH_4^+ in leachates from a forest soil. Whereas, an extremely small fraction of urea-N applied at the same rate was recovered in leachates as NH_4^+. In the same experiment higher rates of urea application resulted in 50-75% of the N applied being recovered as NH_4^+. This work by Overrein (1971) demonstrated the ability of and extent to which a forest soil might immobilize urea fertilizer applications. Mitsui (1967) reported that N immobilization from urea fertilization reflected the ability of urea to self-polymerize as well as form complexes with soil organic constituents, rendering the N from urea less susceptible to leaching.

In addition to the priming effect, whereby fertilizer additions stimulate increased mobilization of NH_4^+, fertilizer N applications appear to stimulate soil microbial activity which can result in the release of water-soluble organic N. In this experiment water-soluble organic N was released equally, following additions of either urea or ammonium sulfate (Figure 38).

Not only was water-extractable organic N affected by fertilizer additions, water-extractable total C was also increased in response to N fertilization. But unlike the similarity in response of the organic N component to both urea and ammonium sulfate additions, water-extractable total C was affected to a very large extent by urea additions and to a lesser extent by additions of ammonium sulfate. It is suggested from the results of this study that urea fertilization resulted in the dispersion of soil colloids following the decrease in soil acidity associated with applications of this N source. The dispersion of colloidal organic materials results in a direct increase in exposed surface area to solubilizing influences of water and the net effect of such dispersion is seen in increased values for soluble C. The nature and structure of the soil organic colloidal materials which appear to be so radically affected by the decreased acidity associated with urea fertilization has been examined in detail over many years by Schnitzer (1969). This researcher studied fulvic acids extracted from the B2h horizons from Spodosols, and from his studies concluded that: (1) Humic and fulvic acids were not single molecules but molecular associations of phenolic and benzene carboxylic compounds which he labelled "building blocks." (2) These "building blocks" appeared to be held together by weak linkages, mainly hydrogen bonds. (3) These acids also aggregated into linear, flexible polyelectrolytes at low pH values but dispersed under less acid conditions, because of increased dissociation of functional groups.

Mechanical shaking of soil and water achieved a similar dispersive effect in this current study. When ammonium sulfate treated soil is extracted with water, or any sample is extracted with N KCl, the soil-water suspension has a relatively high concentration of a strong monovalent cation. The effect of the monovalent cation in the soil suspension is to replace or exchange protons (H^+) from the organic colloidal surfaces with the cation in suspension, resulting in an increase in acidity. When left to stand, these cation saturated suspensions flocculate rather than disperse as in urea amended soil. The increase in acidity from such treatments also results in a decrease in cation exchange capacity and therefore many monovalent and divalent cations may be released into solution.

The decrease in soil acidity brought about by urea fertilization is, therefore, in direct contrast to the effect on soil acidity of ammonium sulfate additions, or extraction of soil with N KCl.

The effects described by Schnitzer (1977) confirm earlier findings of Ogner (1972) who reported the characteristic decrease in acidity and increase in soluble C following urea applications to forest litter materials. The dispersive effects found by Schnitzer and described from the results of this study might indirectly cause a reduction in stability of surface soil structure as a result of the leaching of readily soluble organic matter to a deeper mineral horizon. The increase in soluble C may provide additional energy to soil heterotrophic microbial populations, enabling them in turn to immobilize both C and N. This increased activity can also result in accelerated N transformations and increased availability of mineral forms of N. Simultaneous increased availability of N, P, and cations could result in greatly increased plant uptake of the three classes of nutrients. The C:N ratio at which mineral N will be available for plant uptake has been defined for a number of soil-plant associations. A ratio of 10:1 was mentioned by Alexander (1977) as being the threshold below which mineral N becomes available for plant uptake. This value of 10:1 appears lower than necessary for N to be available to the tree crop on the Wauchula fine sand of this study. The A2 horizon had the lowest ratio of all horizons at 24:1 and the A1 had a ratio of 31:1. However, if the C:N ratio is considered for the soil extracts, the A2 had a C:N ratio of 10:1 and the A1, 12:1 (Table 16). Nitrogen fertilizer inputs will, most likely, be immobilized by soil microbes until the C:N ratio approaches that ratio which is found in microbial cells. This ratio has been reported to be near 10:1 (Alexander, 1977).

If a regression of the C:N ratio relationships in Figure 50 is projected back to coincide with a soil C:N ratio of 10:1, then a corresponding solution C:N ratio is 6:1 for favorable N surplus for plant growth. No doubt microorganisms will be able to exploit available N more readily than higher plants and therefore mineralized N will be subject to microbial immobilization as well as to plant uptake. One N transformation process to be considered later is denitrification, for which it has been suggested (de Haan and Zwerman, 1976) that the C:N ratio in solution be close to 1.3:1 for optimum reduction of NO_3^- and NO_2^- to N_2.

Nitrification

The critical substrate for the autotrophic or heterotrophic conversion of NH_4^+ to $NO_2^- + NO_3^-$ is the supply or rate of supply of NH_4^+. From this study it can be clearly seen that following N fertilization with either urea or ammonium sulfate the supply of NH_4^+, at least initially, is non-limiting. But NO_3^- levels were very low at all times. The many conditions which might account for the observed low NO_3^- levels have been reviewed earlier. Contrary to expectations, ammonium sulfate additions resulted in an early pulse of NO_3^- from the forest floor (Figure 33). One explanation for this observation might be that low levels of NO_3^- are found in the forest floor prior to fertilization. The addition of ammonium sulfate, followed by a heavy rainfall, results in a more rapid elution of NO_3^- from plots treated with ammonium sulfate. The NO_3^- is generally extremely mobile, but it must be paired with a cation to provide electro-neutrality in the soil solution. Ammonium sulfate additions as mentioned previously resulted in a greater concentration of cations in solution and perhaps provided more readily the conditions for ion pairing. Nitrate can be held electrostatically to colloidal surfaces and when sulfate ($SO_4^{=}$) was added to the system NO_3^- on colloidal surfaces would be exchanged for $SO_4^{=}$. In a lysimeter study, Overrein (1971) found a similar increased NO_3^- level in leachates following an application of ammonium chloride fertilizer at the rate of 500 kg $N.ha^{-1}$, compared to NO_3^- levels found in leachates from urea treated soil. However, Sarigumba et al. (1976) reported a greater increase in NO_3^- levels when urea was applied at 448 kg $N.ha^{-1}$ to lysimeter pots than for ammonium sulfate applied at the same rate.

Urea applications at 400 kg $N.ha^{-1}$ resulted in a small increase in NO_3^- levels after 128 days, indicating by this incubation phase that conditions for nitrification were improved by this fertilizer addition.

Water-Extractable Cations and Phosphorus

The effects of the two N sources, ammonium sulfate and urea, on the subsequent exchange reactions has been discussed with respect to the change in soil pH. The outstanding nutrient fluxes were from the forest floor in response to ammonium sulfate applications. Sarigumba et al. (1976) also reported larger increases in the cation content of leachates following ammonium sulfate applications than from urea application. Since the NH_4^+ from ammonium sulfate is replacing monovalent and divalent cations in the surface horizons, this indicates that the basic cations are not very tightly held on the exchange sites. The lowering of the pH associated with the ammonium sulfate additions would also indicate that NH_4^+ was replacing protons (H^+) on the exchange complex. The importance of the forest floor as a source of water-extractable cations following ammonium sulfate application is demonstrated in Table 28. In this table, total cations in the soil profile do not appear to change during the two days following fertilization, and monovalent cations are readily extractable from all horizons with mineral horizons contributing more total cations than the forest floor. Total water-extractable cations increased curvilinearly in response to added ammonium sulfate. The curvilinear increase was also reflected in the divalent cations Ca and Mg (Figure 54 and Table 29). The linear relationship between level of ammonium sulfate and extractable cations is also quite strong. Total water-extractable cations are related to ammonium sulfate fertilizer level in the following regression.

$$\text{TOT Cat}^{1} = 17.4 + 0.207\ (\text{A/S rate})^{2}$$
$$R^2 = 0.97$$

The linear regression between Ca + Mg and ammonium sulfate application was also well defined

$$\text{Ca} + \text{Mg}^{3} = 2.2 + 0.122\ (\text{A/S rate})^{4}$$
$$R^2 = 0.98$$

---

[1] Total water-extractable cations.

[2] Rate of application of ammonium sulfate.

[3] Water extractable calcium plus magnesium.

[4] Rate of application of ammonium sulfate.

Table 28. Water-extractable cations 2 days after fertilization with ammonium sulfate.

Horizon	Al	Ca	Mg	K	Na	Tot.[1] Cat.
	---------------	---------------	---------------	kg.ha^{-1}	---------------	---------------
				Control Plots		
FF	1	2	2	9	11	25
A1	0	3	0	9	26	38
A2	0	3	0	15	59	77
B2h	6	2	0	8	26	42
				Ammonium Sulfate (200 kg N.ha^{-1})		
FF	1	16	8	18	9	52
A1	1	3	0	9	37	50
A2	5	0	0	8	53	66
B2h	4	0	0	5	27	36
				Ammonium Sulfate (400 kg N.ha^{-1})		
FF	1	36	18	39	14	110
A1	0	0	0	16	40	56
A2	0	0	0	14	75	89
B2h	4	0	0	8	28	40

[1] Tot. Cat. = Total of Al + Ca + Mg + Na + K.

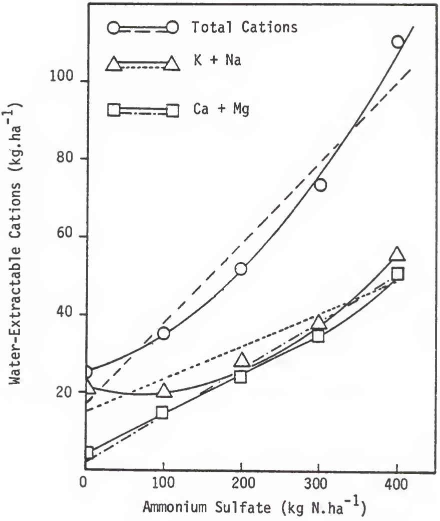

Figure 54. Water-extractable total cations, Ca + Mg, and K + Na in the forest floor 2 days after fertilization with ammonium sulfate.

The linear relationship between K + Na and ammonium sulfate level was

$$K + Na^{1} = 15.2 + 0.086\ (A/S\ rate)^{2}$$
$$R^{2} = 0.93$$

Table 29. Total water-extractable cations Ca + Mg and K + Na from the forest floor, two days after fertilization with ammonium sulfate.

Ammonium sulfate (kg N.ha^{-1})	Ca + Mg (kg.ha^{-1})	K + Na (kg.ha^{-1})	Total cations (kg.ha^{-1})
0	4	21	25
100	15	20	35
200	24	28	52
300	35	38	73
400	55	55	110

Figure 54 shows that monovalent cations were more readily exchanged at low levels of fertilization and that water-extractable Ca+Mg increased relative to K + Na with increasing levels of ammonium sulfate application. At 400 kg.ha^{-1} of ammonium sulfate, monovalent and divalent cations contributed equally to the cation content in the forest floor. The mineral horizons contained mostly monovalent cations, K and Na, with the major contribution from Na, two days after fertilization.

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[1] Water extractable potassium plus sodium.

[2] Rate of application of ammonium sulfate.

Urea fertilization resulted in less mobilization of cations from the forest floor, and this was discussed earlier in terms of an increase in cation exchange capacity (CEC). The relationship between level of urea fertilization and water extractable cations is not as well defined as for ammonium sulfate applications (Table 30). Monovalent cations, and in particular sodium, predominate in the water extracts of the mineral horizons. This further supports the concept of increased CEC, because divalent cations would be more tightly held than the monovalent ones, hence the reduced amount of divalent cations in water extracts.

Crane (1972) found that K was the predominant cation in leachates following urea fertilization of soils in the Pacific Northwest. This basic difference perhaps reflects the maritime environment of peninsular Florida as sodium would be constantly added in aerosol deposition and in rainfall.

Water-extractable Al was found mainly in the B2h horizon with some extracted from the A2 horizon as well. Schnitzer (1969) found that Al and Fe formed the most stable complexes with fulvic acid extracted from a B2h horizon. Aluminum, with its ability to form strong bridging bonds between organic colloids, would therefore be very important in stabilizing the organic components of Spodosols. Because Al is likely to be strongly bound to colloidal surfaces, it explains the low Al levels found in water-extracts of Wauchula fine sand horizons.

Phosphorus appeared to be mobilized by fertilization, whether by ammonium sulfate or urea, perhaps reflecting increased mineralization of organic P. The A1 and A2 horizons contained the major part of water-soluble P and there appeared to be leaching of P from the A1

Table 30 . Water-extractable cations 2 days after fertilization with urea.

Horizon	Al	Ca	Mg	K	Na	Tot. Cat.[2]
	---------------------------kg.ha^{-1}					
			Control Plots			
FF[1]	1	2	2	9	11	25
A1	0	3	0	9	26	38
A2	0	3	0	15	59	77
B2h	6	2	0	8	26	42
			Urea (200 kg N.ha^{-1})			
FF	1	0	0	1	4	6
A1	0	0	0	10	20	30
A2	0	4	4	17	48	73
B2h	7	0	0	8	25	40
			Urea (400 kg N.ha^{-1})			
FF	1	1	0	2	7	11
A1	0	0	0	7	33	40
A2	0	0	0	6	55	61
B2h	2	0	0	4	26	32

[1] FF = Forest floor.

[2] Tot. Cat. = Total of Ca + Mg + Al + K + Na.

to the A2 (Figure 46). Burger (1979) suggested that increased mineralization following site preparation was partly responsible for elevated P levels in intensively prepared sites. Nitrogen fertilization appeared also to provide the necessary stimulation of decomposition and mineralization of soil organic matter, to result in elevated levels of P.

Gaseous Losses

There were two important components of gaseous N losses from the fertilized slash pine plantation. Initially NH_3 volatilization accounted for gaseous N evolution, particularly following urea applications. Later denitrification loss as measured by N_2O flux from the forest floor, was the main component of gaseous N loss.

Ammonia Volatilization

Ammonia volatilization reflected the rate of hydrolysis of the urea fertilizer additions, as mentioned earlier in the discussion on ureolysis. Major volatilization losses occurred in the first 16 days, and NH_3 losses from sprayed applications of urea applied at 100 and 200 kg $N.ha^{-1}$ were greater than losses from applications of prilled urea at these levels.

The exponential decay in NH_3 losses, as expressed in the regression using cumulative throughfall as the independent variable, suggests that applications of urea should not be made when chances of a prolonged rain-free period are high.

The 9 kg NH_3-N.ha^{-1} measured cumulative loss from the 300 kg urea-N.ha^{-1} application represents 3% of applied N and is a low percentage loss compared with the results of Sarigumba (1974) and Crane (1972), but compared favorably with the 3.5% loss reported by Overrein (1968) for high levels of applied urea. It might be argued that the static diffusion traps used to measure NH_3 loss underestimate total volatile NH_3 losses, but Crane (1972) in a comprehensive series of experiments concluded that alternative continuous flow traps suffer from the risk of a major overestimation of these losses.

Ammonium sulfate applications did result in some small increase in NH_3 loss, but the increase in loss rate was measured only during two days following fertilizer application (Table 5).

Denitrification

The loss of gaseous N in the form of N_2O occurred for the entire 128 days on which observations were made. There was considerable variation between replicate traps for the measurement of background levels of N_2O evolution from unfertilized field plots. The average rate of N_2O-N evolution from untreated controls from both field experiments #2 and #3 was 1.4 ± 1.0 g N_2O-N.ha^{-1}.day^{-1}. Increasing the number of field replications of control traps would improve the standard deviation about this value.

Chemo-Denitrification

The only evidence for some component of chemo-denitrification in N_2O evolution was on day 29 from field experiment #2 when a significant recording of N_2O flux was made from plots treated with ammonium sulfate at 400 kg $N.ha^{-1}$. No elevated levels of N_2O were recorded on this date from the urea plots treated at the same rate. The decrease in soil acidity which occurred following urea fertilization was considered more likely to result in nitrification than from soils amended with ammonium sulfate. However, some NO_2^- + NO_3^- was found immediately after fertilization with ammonium sulfate (Figures 33 and 34) and these data suggest that ammonium sulfate applications result in levels of NO_2^- + NO_3^-, initially, which are not found when urea is applied. Chemo-denitrification could be instantaneously reducing part of the NO_2^- or NO_3^- by any or all of the reactions proposed for chemical reduction of NO_2^- (Allison, 1963; Broadbent and Clark, 1965) or the reduction of NO_3^- in the presence of reduced iron (Fe^{++}) (Chao and Kroontje, 1966).

Chemo-denitrification is suggested to be contributing to NO_3^- loss because these reactions are known to occur in acidic conditions.

The biological process of denitrification would be restricted at soil pH values < 5. However, Gilliam and Gambrell (1978) were able to measure loss of nitrate in Atlantic coastal plain topsoils and their acidic subsoils. They suggested that the soil microflora in these soils had adapted to denitrify in acidic (< pH 5) conditions. The conditions found in the experiments conducted by Gilliam and Gambrell (1978) would also be suitable for chemo-denitrification to take place.

Biological Denitrification

The requirements for biological denitrification are the absence of oxygen and the presence of oxidized N compounds, NO_3^- as a primary example, to provide electron acceptors for the process. In addition an external energy source (C) is required. Gilliam and Gambrell (1978) found denitrification rate, especially at low temperatures, responded to additions of C, thus confirming that when C is in short supply denitrification may be limited.

In experiments conducted on acid sandy soils the supply of NO_3^- or the rate of NO_3^- formation appears to be the critical determinant in the overall supply of ingredients for denitrification. Urea applications at 400 kg $N.ha^{-1}$ result in elevated soil pH, increased carbon in solution (Table 35 and Figure 47) and abundant NH_4^+. So, firstly, nitrification could occur and the NO_2^- and NO_3^- formed could be instantaneously reduced by both chemical and biological pathways. An incubation period appeared to be required following the application of urea at 400 kg $N.ha^{-1}$, before N_2O was detected from these plots. This suggests that the microflora (both heterotrophic and autotrophic) capable of nitrifying was expanding in response to new substrate conditions. Subsequently, the NO_3^- so formed was reduced giving rise to the N_2O evolution. In this case I suggest a biological pathway contributes to denitrification losses because of the long delay (56 days) before significant N_2O was detected. However, it is more realistic to suggest that under the relatively harsh soil acidity conditions, that both chemo- and biological denitrification are contributing to N_2O evolution. In addition, nitrification was recently suggested as a potential pathway for N_2O evolution (Bremner and

Blackmer, 1979). These researchers suggested that N_2O could be evolved as an intermediate in the biological oxidation of $NH_4^+ \rightarrow NO_3^-$.

Consequences of N_2O Evolution

Nitrous oxide is a recognized intermediate in the reduction of NO_3^- and NO_2^- to N_2. Nitric oxide (NO) has been identified in the sequence

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$

but is generally considered to be insignificant. However, *Terry (1979) has noted that in the gas-chromatographic technique employed to analyze for N_2O, the separation of a NO peak from a N_2O peak is not possible. Therefore,we in fact could be measuring NO + N_2O.

Of primary importance in the calculation of total denitrification is the ratio of N_2:N_2O. The values for this ratio have been discussed in the review section, and the value of 10:1 is considered a useful ratio for calculation of total denitrification. This value of 10:1 was used by Messer (1978) in calculating the denitrification component within a nitrogen budget for peninsular Florida. Calculated values for this ratio ranged between 100:1 and 1:4 (Gilliam et al., 1978) for Californian soils and from greater than 100:1 to 10:1 (**Krottje, 1979) for several soils from Florida.

Even though the high rate of N_2O evolution was recorded for just 2 days under other conditions of less extreme rainfall this peak loss rate could be maintained for several days. However, it appears that any significant rainfall event has the potential to reduce peak N_2O evolution, possibly by leaching NO_2^- and NO_3^- deep into the soil profile.

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*Note: Terry, R.E. Personal communication.

**Note: Krottje, P. Personal communication.

Average daily N_2O losses from field experiments #2 and #3 were calculated by integrating the area under the curves for periodic N_2O values (Figures 52 and 53). The low values in average daily N_2O flux from field experiment #2 compared with values from #3 (Tables 31 and 32) can perhaps be explained by the long period of rain-free weather at the commencement of #2, which resulted in little or no N_2O evolution for more than 20 days. Table 33 summarizes the consequences of the $N_2:N_2O$ ratio on total denitrification losses. For the most likely ratio of 10:1 losses by denitrification for 100 days immediately following fertilization are well under 1% of applied N except for ammonium nitrate applied at 200 kg $N.ha^{-1}$, where the projected loss of 6.46 kg $N.ha^{-1}$ represents a 3.2% loss of applied N in 100 days (Figure 55). If this rate of denitrification from ammonium nitrate treated plots persists for the whole year then the loss would be 24 kg or > 12% of applied N.

The greater percentage loss from ammonium nitrate fertilizer applications is evidence for a biological pathway of denitrification. This is reinforced by the fact that ammonium sulfate applied at the same time as the ammonium nitrate does not result in any large increase in projected total N loss. It would appear therefore, that it was necessary to apply 400 kg urea-$N.ha^{-1}$ before amelioration of the soil environment was achieved to allow nitrification and subsequent denitrification.

Table 31 . Loss of N_2O from field experiment #2 during 128 days.

Treatment	Total N_2O-N loss in 128 days	Average daily loss of N_2O-N
	($g.ha^{-1}$)	($g.ha^{-1}$)
Control (9)[1]	76	0.59
Ammonium sulfate (200)	100	0.78
Ammonium sulfate (400	151	1.18
Urea (200)	90	0.70
Urea (400)	434	3.39

[1] ( ) Rate of application of fertilizer (kg $N.ha^{-1}$).

Table 32. Loss of N_2O from field experiment #3 during 85 days, from three fertilizers applied at 200 kg $N.ha^{-1}$.

Treatment	Total N_2O-N loss in 85 days	Average daily loss of N_2O-N
	($g.ha^{-1}$)	($g.ha^{-1}.d^{-1}$)
Control	97	1.14
Ammonium sulfate	167	1.96
Urea	131	1.54
Ammonium nitrate	493	5.80

Table 33 . Consequences of N_2:N_2O ratios on total denitrification losses for a 100 day period.

Treatments (experiments #2 and #3)	Average daily loss of N_2O-N	100 day loss of N_2O-N	100 day N loss for various N_2:N_2O ratios 1:1	5:1	10:1	20:1	100:1
	$g.ha^{-1}$	$g.ha^{-1}$	----------kg $N.ha^{-1}$-----------				
Control (0)[1]	0.865	86.5	0.17	0.52	0.95	1.82	8.73
Ammonium sulfate (200)	1.37	137	0.27	0.82	1.51	2.88	13.83
(400)	1.18	118	0.24	0.71	1.30	2.48	11.92
Urea (200)	1.12	112	0.22	0.67	1.23	2.35	11.2
(400)	3.39	339	0.68	2.03	3.73	7.12	34.2
Ammonium nitrate (200)	5.80	580	1.16	3.48	6.38	12.18	58.6

[1] ( ) rate of fertilizer N application (kg $N.ha^{-1}$).

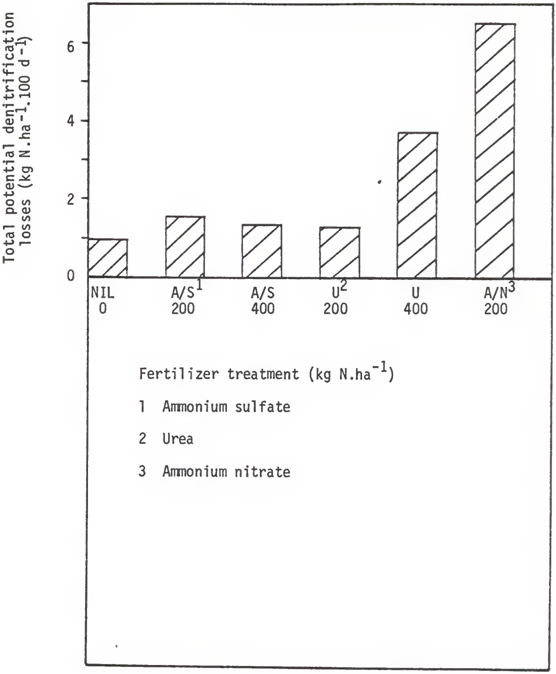

Figure 55. Total potential denitrification losses using a N_2:N_2O ratio of 10:1 during 100 days following N fertilization.

If the $N_2:N_2O$ ratio is closer to 1:1, then total denitrification becomes quite insignificant. If the ratio is close to 100:1 then denitrification becomes a very significant sink for fertilizer N. Measurements of the ratio $N_2:N_2O$ suggest that a ratio near 100:1 is possible (*Krottje, 1979).

The projected total denitrification losses from ammonium sulfate applications appear to be independent of amount of fertilizer N applied. This would suggest that an intermediate process such as nitrification was rate limiting for denitrification. Even at the $N_2:N_2O$ ratio of 100:1 the projected loss from ammonium sulfate applications (13.83 and 11.92 kg $N.ha^{-1}$) was an average 4.9% loss of applied N in 100 days.

Mead (1971) was unable to account for approximately 50% of ^{15}N ammonium sulfate applied to a slash pine ecosystem at the end of 19 months (570 days). If 10:1 is a realistic ratio for $N_2:N_2O$ in total denitrification then for an application of 224 kg $N.ha^{-1}$ Mead could expect to lose 5.7 x 1.5 = 8.5 kg $N.ha^{-1}$ during 570 days. The 8.5 kg $N.ha^{-1}$ loss would represent a 3.8% loss of applied N. This would leave 46% to be accounted for by leaching losses. If the $N_2:N_2O$ ratio was closer to 100:1 then the total denitrification loss in Mead's (1971) study would be 39% of the applied N. An intermediate ratio of (20:1) for $N_2:N_2O$, which is not at all unrealistic, would account for 8.2% of the applied N.

In field experiment #2, once a peak rate of N_2O evolution had been measured, one significant rainfall event was sufficient to result

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*Note: Krottje, P., 1979, personal communication.

in lower subsequent N_2O flux. This would suggest that leaching losses are likely to be more important than gaseous losses for fertilizer N applications to a flatwood forest on a sandy Spodosol. These denitrification results suggest that if nitrification was higher, or nitrate-rich fertilizers are applied, and if leaching was prevented, then the N losses from this process could be much more significant. Soil series within the flatwoods ecosystem with a less permeable soil profile could be induced to evolve more significant levels of N_2O and N_2.

The total gaseous losses from NH_3 and total denitrification need be considered for urea applications. Losses from NH_3 amounted to 3% of a 300 kg $N.ha^{-1}$ application whilst denitrification calculated for a $N_2:N_2O$ ratio of 10:1 during 100 days after fertilization is likely to represent < 1% of applied N. However, if a $N_2:N_2O$ ratio of 100:1 was used to calculate total denitrification then denitrification losses from urea applied at 200 kg $N.ha^{-1}$ would be 11 kg $N.ha^{-1}$ or a 5.5% loss and 34 kg $N.ha^{-1}$ or 8.5% of a 400 kg $N.ha^{-1}$ application of urea.

SUMMARY AND CONCLUSIONS

The products of nitrogen transformations following application of fertilizer N to a 23-year-old slash pine plantation were monitored in order to evaluate the effects of sources and rates of application on the subsequent soil reactions.

Measurements of NH_3 volatilization and N_2O evolution were carried out in order to compare the relative roles of each gaseous N loss and to contrast them both with potential losses from leaching.

Urea and ammonium sulfate were applied to the forest floor at five levels, 0, 100, 200, 300 and 400 kg $N.ha^{-1}$, in a water solution by spraying. Rainfall and throughfall were monitored throughout the experimental period.

Soil samples and NH_3 gas samples were taken from the treatment plots during 128 days following fertilizer application.

One year later, in two separate installations within the same experimental locations, assessments of potential denitrification losses were made. This was achieved by monitoring N_2O evolution from urea and ammonium sulfate at three rates in the first installation, and from urea, ammonium sulfate, and ammonium nitrate in a second installation.

The effects of N fertilization, namely, changes in soil acidity, mobilization and enhanced mineralization of organic soil components, as well as reactions with soil cations and phosphorus, were assessed by routine periodic soil sampling following fertilization. The results from these studies lead to the following conclusions.

(1) Hydrolysis of applied urea fertilizers was extremely rapid, and this initial transformation occurred principally in the forest floor.

(2) Ammonia volatilization resulting from ammonium sulfate applications was found to be negligible when compared with the losses associated with urea applications. Ammonia volatilization following urea applications amount to 3% of the applied N, and this amount was controlled to a great extent by the pattern of rainfall following urea fertilization. The losses measured in this study compared favorably with those recorded in other coniferous ecosystems following urea fertilization.

(3) Soil acidity was decreased by as much as two pH units following applications of urea, and the increased pH value was steadily reduced during 128 days. Applications of ammonium sulfate increased soil acidity values by about one unit; however, in this case the change in acidity lasted for fewer days than when urea was applied.

(4) The reduction in water-extractable NH_4^+ and basic cations Ca, Mg, Na, and K from the soil was associated with the decrease in soil acidity following urea fertilization. Ammonium sulfate applications resulted in an increased concentration of NH_4^+ and cations, probably due to decreased cation exchange capacity associated with increased soil acidity following fertilization with this source of N.

(5) Urea and to a lesser extent ammonium sulfate fertilization resulted in more water soluble C, thus increasing the energy substrate for heterotrophic decomposition, ammonification, nitrification, and denitrification.

(6) Changes in water-extractable total N reflected the rapid flux in water-extractable NH_4^+, since NH_4^+ was the dominant N form in solution following ammonium sulfate or urea additions. Soil total N measured the gross effects on N concentration following fertilization but was relatively insensitive as an index of N movement in the soil profile.

(7) Changes in soil acidity, contents of readily extracted C, total N, NH_4^+, NO_3^-, C:N ratios, cations, and P were well predicted from linear models using combinations of fertilizer treatment and time since application. Cumulative rainfall substituted for time since application of fertilizers in the predictive equations resulted in equally significant performance of the models.

(8) In spite of fertilizer N addition and accompanying improvements in soil conditions for nitrification following urea fertilization, NO_3^- concentrations were very low. The low NO_3^- levels were the net result of low nitrification, potentially more rapid assimilation and disimilation by higher plants as well as microbes, and higher leaching losses.

(9) Denitrification, when measured by N_2O fluxes and a ratio of $N_2:N_2O$ of 10:1, resulted in low N losses throughout the experimental period. Additions of urea at 400 kg $N.ha^{-1}$ and ammonium nitrate at 200 kg $N.ha^{-1}$ resulted in denitrification losses close to 1% of the applied N.

(10) If a N_2:N_2O ratio of 100:1 is used to calculate denitrification losses, which is realistic, then up to 29% of applied N from ammonium nitrate was lost by this process during 100 days following fertilization.

(11) Leaching losses stemming from regular tropical summer storm events (500 mm rainfall in 50 days) rather than gaseous losses are likely to be responsible for the unaccounted for N in this pine ecosystem.

APPENDICES

APPENDIX A

SOIL PROFILE DESCRIPTION

Table 34 . Soil profile descriptions for Wauchula fine sand.

Horizon	Depth	Description
L	14-4 cm	Recent pine litter mixed with fronds of saw palmetto.
F O_1	4-0.5 cm	Fragments of semi-decayed litter materials; abrupt boundary.
H O_{11}	0.5-0 cm	Black and very dark gray particles of decayed litter; abrupt boundary.
A1	0-5 cm	Very dark gray (10 YR 3/1) fine sand; very friable; single grain; common medium and fine roots; abrupt wavy boundary.
A2	5-28 cm	White (10 YR 8/1) fine sand; friable; few indistinct pinkish gray (7.5 YR 7/2) mottles, single grain: few roots; abrupt wavy boundary.
B21h	28-32 cm	Black (10 YR 4/3) fine sand; friable; few roots; clear wavy boundary.
B22h	32-39 cm	Dark brown (7.5 YR 3/4) fine sand; firm when moist, hard when dry; weakly cemented; few dead fine roots; clear wavy boundary.
B3	39-52 cm	Brown (10 YR 4/3) fine sand; common clear dark brown (7.5 YR 3/4) mottles; friable; few dead roots; clear wavy boundary.
A'2	52-71 cm	Pale brown (10 YR 6/3) fine sand; indistinct yellowish-brown (10 YR 5/6) mottles; single grain; friable; clear wavy boundary.
B'1t	71-95 cm	Yellowish-brown (10 YR 5/4) fine sandy loam; distinct dark brown (7.5 YR 3/4) along root channels; weak medium granular; friable; gradual wavy boundary.
B'21tg	95-108 cm	Light gray (2.5 YR 7/2) sandy clay loam; weak medium subangular common distinct red (2.5 YR 4/8) and strong brown (7.5 YR 5/8) plinthitic mottles;
*B'22tg	108-142 cm	Gray (5 YR 6/1) sandy clay loam; common, fine, distinct, yellowish-brown (10 YR 5/8) mottles; moderate medium subangular blocky; friable; gradual irregular boundary.

Table 34. (Continued)

Horizon		Description
*B'3g	108-142 cm	Gray (5 Y 6/1) sandy loam; common, fine, faint, light gray (5 YR 7/2), few, fine, prominent red. (2.5 YR 4/8), and few large distinct, reddish-yellow (7.5 YR 6/8) mottles; weak fine subangular blocky; friable; gradual irregular boundary.
*Cg	170-201 cm	Gray (10 YR 6/1) sandy loam; few to common, fine red (10 YR 4/8), few to common, fine, prominent, yellowish-red (5 YR 4/8), and few to common, fine, distinct, strong brown (7.5 YR 5/8) mottles; massive, to angular blocky; friable.

APPENDIX B

TABLES OF SUPPORTING DATA AND STATISTICAL DESIGNS

Table 35. Soil extract pH changes following fertilization.

Horizon	DST[1]	Fertilizer source				
		Nil	Ammonium sulfate		Urea	
		Rate of application (kg N.ha^{-1})				
		0	200	400	200	400
FF[2]	0	3.98	3.96	3.94	4.11	4.15
	2	4.15	3.57	3.55	5.84	5.76
	4	4.13	3.56	3.58	5.16	6.31
	12	4.16	3.81	3.82	5.21	5.91
	32	4.18	4.05	4.36	4.57	5.68
	128	4.03	3.83	3.84	4.22	4.62
A1	0	4.50	4.34	4.40	4.46	4.54
	2	4.56	4.21	4.31	4.98	4.93
	4	4.70	4.29	4.19	4.78	5.29
	12	4.46	3.97	4.14	4.71	5.20
	32	4.30	4.14	4.38	4.32	4.91
	128	4.26	4.14	4.20	4.31	4.33
A2	0	4.84	4.96	4.95	4.96	4.80
	2	4.85	4.70	4.87	5.08	5.30
	4	5.13	4.90	4.92	5.34	5.55
	12	4.86	4.84	4.82	4.97	4.95
	32	4.50	4.47	4.50	4.49	4.63
	128	4.43	4.40	4.38	4.43	4.43
B2h	0	4.52	4.51	4.49	4.55	4.67
	2	4.48	4.58	4.47	4.68	4.74
	4	4.72	4.66	4.71	4.80	4.85
	12	4.50	4.47	4.50	4.55	4.53
	32	4.34	4.17	4.23	4.23	4.35
	128	4.35	4.18	3.98	4.37	4.34

[1] Days since fertilization.

[2] Forest floor.

Table 36. Soil total nitrogen concentration in each horizon following fertilization.

Horizon	DST[1]	Fertilizer source			Urea	
		Nil	Ammonium sulfate			
		Rate of application (kg N.ha^{-1})				
		0	200	400	200	400
		ppm (ODW)				
FF[2]	0	7595	8653	8573	7137	7227
	2	9990	11490	17385	12930	14930
	4	8110	13920	15760	10500	12500
	8	6210	12560	14080	11650	15940
	12	8034	11590	11540	11746	15300
	16	10650	12360	15750	13890	13180
	21	7770	6620	9270	9540	11250
	32	8069	8160	10340	9170	11110
	64	10560	8460	11550	8690	10450
	128	6990	9030	9310	9660	9660
A1	0	271	519	455	366	461
	2	242	407	375	441	539
	4	322	539	733	458	556
	8	306	483	458	436	411
	12	412	453	318	410	494
	16	398	624	559	478	564
	21	409	676	608	442	865
	32	298	643	558	398	497
	64	436	852	572	619	471
	128	317	515	392	325	444

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[1] Days since fertilization.

[2] Forest floor.

Table 36. (Continued)

Horizon	DST[1]	Fertilizer source				
		Nil	Ammonium sulfate		Urea	
		Rate of application (kg N.ha^{-1})				
		0	200	400	200	400
		ppm (ODW)				
A2	0	75	73	82	85	85
	2	64	64	78	103	109
	4	86	94	116	81	117
	8	83	99	93	101	109
	12	71	80	77	84	131
	16	115	112	147	95	128
	21	104	92	96	234	94
	32	71	90	95	80	106
	64	103	119	134	132	114
	128	101	114	123	105	140
B2h	0	550	476	533	589	530
	2	619	446	425	616	581
	4	485	509	449	615	566
	8	541	416	503	556	483
	12	591	337	479	581	668
	16	521	581	546	709	626
	21	587	553	382	591	627
	32	422	424	529	559	568
	64	515	483	565	616	614
	128	641	563	548	584	524

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[1] Days since fertilizer treatment.

Table 37. Concentration of NH_4^+-N in water and N KCl extracts of the forest floor.

DST[1]	Fertilizer source				
	Nil	Ammonium sulfate		Urea	
	Rate of application (kg N.ha^{-1})				
	0	200	400	200	400
	Water Extractable NH_4^+-N				
	------------- ppm (ODW) -------------				
0	26				
2	34	2350	7605	1288	2325
4	24	2401	3640	391	704
8	19	2044	4375	628	1114
12	35	1333	2550	498	867
16	23	1226	1675	596	613
21	35	18	51	29	33
32	16	165	303	221	424
64	26	43	52	105	140
128	0	4	5	51	165
	N KCl Extractable NH_4^+-N				
0	198				
2	322	3470	11199	6889	10859
4	204	3540	5370	5420	9760
8	132	3010	6440	8717	15463
12	418	1963	3760	6906	12032
16	214	1806	2467	8261	8498
21	290	27	76	393	445
32	146	243	447	2063	5882
64	182	64	77	1454	1930
128	0	7	8	690	2287

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[1] Days since fertilizer treatment.

Table 38. Transformations of soil chemical parameters.

TERM	= Log	(Soil Parameter)
LSTN	= Log	(soil total N)
LEXTN	= Log	(water extract total N)
LEXPH	= Log	(water extract pH)
$LEXNH_4N$	= Log	(water extract NH_4^+-N)
$LEXNH_4K$	= Log	(N KCl extract NH_4^+-N)
$LEXNO_3N$	= Log	(water extract NO_3^--N)
LEXURN	= Log	(water extract urea-N)
LONWE	= Log	(water extract organic-N)
LCaHA	= Log	(water extract calcium)
LMGHA	= Log	(water extract magnesium)
LKHA	= Log	(water extract potassium)
LNaHA	= Log	(water extract sodium)
LAlHA	= Log	(water extract aluminum)
LTCATHA	= Log	(water extract total cations)
LPHA	= Log	(water extract phosphorus)
LEXTCHA	= Log	(water extract total carbon)
LEXC:N	= Log	(water extract C:N ratio)

Table 39. Terms used in the predictive two-tiered models to analyze soil nitrogen movement.

Model Parameter
Blocks (B)
N Rate (R)
N Source (D)
R × D
Lack of fit (T)[1]
Error (a)
Time since fertilization (DST)
DST × DST
N Rate × DST
N Source × DST
R x D × DST
Lack of fit (T × DST)
Error (b)

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[1] The lack of fit term for the source × rate tier was a term for treatment combination (T), and in the time × source × rate tier was a term for treatment and time (T × DST).

Table 40. Rainfall and cummulative rainfall for field experiments #2 and #3.

	Field Experiment #2			Field Experiment #3		
Date	DST[1] (days)	through fall[2] (mm)	Cumm.[3] T fall (mm)	(days)	through-fall (mm)	Cum. T fall (mm)
4- 8-79	0	0	0			
4- 9-78	1	0	0			
4-11-79	3	19	19			
4-17-79	9	18	37			
4-23-79	15	0	37			
4-25-79	17	0	37			
4-30-79	22	54	91			
5- 1-79	23	0	91	0	0	0
5- 2-79	24	0	91	1	0	0
5- 7-79	29	0	91	6	0	0
5-10-79	32	50	141	9	50	50
5-21-79	43	0	141	20	0	50
5-28-79	50	2	143	27	0	52
6- 1-79	54	56	199	31	56	108
6- 3-79	56	0	199	33	0	108
6- 4-79	57	0	199	34	0	109
6- 7-79	60	0	199	37	0	109
6- 4-79	62	0	199	39	0	109
6-15-79	68	13	212	45	13	122
6-22-79	75	56	268	52	56	178
6-23-79	76	11	279	53	11	189
7- 4-79	87	2	281	64	2	191
7-11-79	94	50	331	71	50	241
7-18-79	101	24	355	78	24	265
7-25-79	108	28	383	85	28	293

[1] Days since fertilizer treatment.

[2] Throughfall measured on field experimental location.

[3] Cummulative throughfall.

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BIOGRAPHICAL SKETCH

David Bruce Boomsma, son of Clifford and Elizabeth Boomsma, was born September 24, 1943, in Adelaide, South Australia. He graduated from Marion High School in December 1962. He attended Adelaide University in 1963 and 1964, and the Australian National University, Canberra, during 1965 and 1966, assisted by a forestry cadetship provided by the South Australian government Woods and Forests Department. In March 1967, he graduated Bachelor of Science (forestry) with Honours, and received the Commonwealth Forestry Book Prize.

From March 1967 to March 1972, he was employed as a forester in plantation management and logging operations for the Woods and Forests Department, at Penola Forest Reserve, South Australia, and from March 1972 to August 1976, as Research Officer in the Research Branch, of Woods and Forests Department, Mount Gambier, South Australia. From August 1976 to the present, he was enrolled at the University of Florida in the Soil Science Department.

David Boomsma is married to Helen Beverley (Sugg) Boomsma and they have two children, Alison Claire, aged 9, and Jonathan David, aged 6.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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